PREPARATION AND PROPERTIES OF SOME ORGANIC-INORGANIC ION-EXCHANGE MATERIALS

ABSTRACT

THESIS

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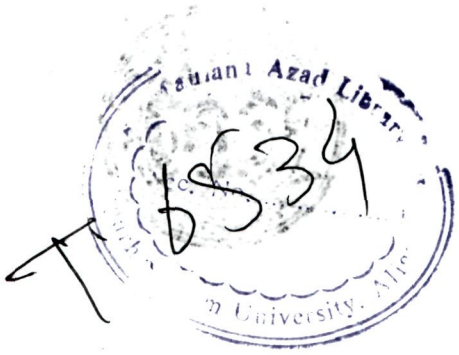

Summary

Abstract

Organic-inorganic Composite Cation-exchange Materials

There has been substantial research on the inorganic ion-exchangers as well as organic resins commonly known as ion-exchange media for the remediation of wastewater containing heavy metal ions as a by product of various industries. However the practical use of organic and inorganic ion-exchange media are still limited by two major obstacles, one of the important limitations of organic resin is its poor thermal and radiation stability than inorganic ion-exchangers and other is the non-reproducible character, less stability in high acidic and basic medium and high cost of inorganic ion-exchangers. Further more inorganic ion-exchangers cannot be used in convenient way in case when the impurities from a large volume of effluent are to be removed. In this connection, research has motivated to the investigators to study of organic-inorganic composite ion-exchangers with better mechanical, chemical, thermal and radiation stabilities, reproducibility and possessing good selectivity for heavy toxic metals, indicating its useful environmental applications. As early as the late 1980s, molecular level combination between organic polymers and inorganic materials has been of interest. The resulting materials i.e., the organic–inorganic composite materials have also attracted a great attention since then in the field of material science because of their unique opportunity to combine the remarkable features of organic compounds with those of inorganic materials. Their applications have also been

explored and reported in the fields of catalyst, coatings, gas permselectivity, fuel cell, chemical sensors, and ion-facilitated transport or ion exchange. Among a wide variety of applications of hybrid materials explored, the ones that possess ion-exchange properties have recently drawn particular interest since ion-exchange is important for a variety of applications such as water treatment, chemical separation, and electrochemical sensing. With these considerations, in our present work two organic–inorganic electrically conducting composite cation-exchange materials based on polypyrrole and polyaniline have been chemically prepared by the sol-gel mixing of organic conducting polymer with the inorganic ion-exchanger precipitates of multivalent metal acid salts, i.e., Th(IV) phosphate and Sn(IV) phosphate, respectively.

Finding of the Work Done

The research work done in the thesis entitled ***"Preparation and properties of some organic-inorganic ion-exchange materials"*** is compiled in six chapters:

Chapter – 1 entitled ***"General Introduction"*** gives a detailed definition and classification of composite materials. A brief history, preparation and properties of polymer matrix composite i.e. organic-organic and organic-inorganic composites, have been discussed. Special interests are focused on electrically conducting composite materials. Historical background of chromatography, types of chromatography in short and particularly ion-exchange chromatography and its recent advances in details have been discussed. A history and development of electrical conduction in materials, electrically conducting polymers especially

polypyrrole and polyaniline, electrically conducting organic-inorganic composite materials and their applications in optics, conductors, sensors and ion-exchangers followed by a comprehensive list of references have been discussed in details. Lastly, this chapter includes the introduction of membranes and electrochemical sensors followed by a comprehensive list of references. Critical reviews of the studies on inorganic ion-exchangers, organic resins, intercalating ion-exchangers, chelating ion-exchangers and '*organic-inorganic*' composite materials used as synthetic ion-exchangers, electrically semiconductors, ion-exchanger membranes, ion-selective electrodes, etc. have also been given based on the literature survey which reveal the some of the novel applications of these materials. Basic principles of organic-inorganic ion-exchangers and ion-selective electrodes and their analytical applications in the literature so far have also been discussed.

Chapter – 2 entitled ***"Preparation and characterization of new and novel 'organic-inorganic' composite cation-exchange materials: polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate"***. The main points of this chapter are the preparation and characterization of two new and novel organic-inorganic cation-exchangers i.e. polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate. Various samples of these two composites of different compositions have been synthesized under various conditions such as different mixing ratios (v/v) at different pH values. The sample of polypyrrole Th(IV) phosphate (S-5) with a Th:P:C:H:N:O (molar composition ratio of 1:2.34:11.77:25.36:2.73:15.21) was prepared by mixing 33.33% pyrrole solution (prepared in toluene) into the white

gel type slurries of Th(IV) phosphate (prepared by mixing a solution of 0.1 M $Th(NO_3)_4.5H_2O$ in 1 M HNO_3 at the flow rate of 0.5 ml min^{-1} to a solution of H_3PO_4 at a temperature of 85 ± 5 °C). Table 1 gives the details of preparation and sample S-5 selected for detail studies. While polyaniline Sn(IV) phosphate composite cation-exchanger with a Sn:P:C:H:N:O (molar composition ratios of 1:3.28:6:24.50:1.07:23.57) was prepared by mixing green color gel of polyaniline (prepared by mixing similar volumes of the solutions of 10% aniline ($C_6H_5NH_2$) and 0.1 M potassium persulphate with continuous stirring by a magnetic stirrer at below 10 °C for half an hour) into the white inorganic precipitate of Sn(IV) phosphate (prepared by mixing 0.1 M stannic chloride solution to an aqueous solution of 0.1 M di-sodium hydrogen orthophosphate (Na_2HPO_4) at pH 1 in different mixing volume ratios). Table 2 gives the details of preparation and sample T-7 selected for detail studies. The resultant gels were kept for 24 h at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was decanted and gel was filtered by suction. The excess acid was removed by washing with DMW and then material was dried in an air oven at 50 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H^+-form by treating with 1 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and the dried at 50 °C. The particles size of range (~ 125 μm) of the material was obtained by sieving and kept in desiccators.

Table 1

Conditions of preparation and the ion-exchange capacity of polypyrrole Th(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratios (v/v)					Appearance of the beads after drying	Na^+ ion exchange capacity (meq dry g^{-1})
	0.1 M $Th(NO_3)_4.5H_2O$ in 1 M HNO_3	H_3PO_4	Digestion time (h)	$FeCl_3$ (0.1 M)	Pyrrole in toluene (33.33%)		
S-1	5	2 (1 M)	4	2	0.30	Blackish granular	1.19
S-2	5	2 (1 M)	24	2	0.30	Blackish granular	0.78
S-3	5	3 (1 M)	4.30	2	0.30	Blackish granular	1.10
S-4	5	2 (2 M)	24	2	0.30	Blackish granular	0.62
S-5	5	2 (2 M)	5	2	0.30	Blackish granular	1.56
S-6	5	2 (2 M)	5	-	-	White sheet	0.72
S-7	-	-	-	2	0.30	Black powder	0.05
S-8	5	2 (2 M)	5	2	0.18	Blackish granular	0.58
S-9	5	2 (2 M)	5	2.5	0.42	Blackish granular	0.27
S-10	5	2 (2 M)	5	2.5	0.60	Blackish granular	0.29
S-11	5	2 (2 M)	5	2.5	0.75	Blackish granular	0.51
S-12	5	2 (2 M)	5	2.5	0.90	Blackish granular	0.31

Table 2

Conditions of preparation of various samples of polyaniline Sn(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratios (v/v)					Appearance of the beads after drying	Na^+ ion- exchange capacity (meq dry g^{-1})
	0.1 M $SnCl_4.5H_2O$ in 4 M HCl	0.1 M Na_2HPO_4 in DMW	pH of the inorganic precipitate	0.1 M $K_2S_2O_8$ in 1 M HCl	10% Aniline in 1 M HCl		
T-1	1	1	1.0	1	1	Greenish granular	1.10
T-2	1	2	1.0	1	1	Greenish granular	1.45
T-3	2	1	1.0	1	1	Greenish granular	0.85
T-4	2	2	1.0	1	1	Greenish granular	0.96
T-5	-	-	-	1	1	Greenish granular	0.20
T-6	2	3	1.0	-	-	White granular	1.12
T-7	2	3	1.0	1	1	Greenish granular	1.96
T-8	1	3	1.0	1	1	Greenish granular	0.58
T-9	1	4	1.0	1	1	Greenish granular	0.45
T-10	3	4	1.0	1	1	Greenish granular	0.72
T-11	2	3	1.0	2	1	Greenish granular	1.20
T-12	2	3	1.0	1	2	Dark green	0.98
T-13	2	3	1.0	2	2	Dark green	1.40
T-14	2	3	1.0	3	2	Dark green	0.92
T-15	2	3	1.0	2	3	Dark green	0.85

The solubility experiment of polypyrrole Th(IV) phosphate composite cation-exchanger (Table 3) showed that the material has reasonable good chemical stability as the results indicated that the material was resistant to 2 M HCl, 2 M HNO_3, and 0.5 M H_2SO_4. This material is completely dissolved in 4 M HCl, 4 M HNO_3, 4 M $HClO_4$, and 2 M H_2SO_4. The chemical dissolution in DMW, alkaline media, $NaNO_3$, NH_3, DMSO, acetone and *n*-butyl alcohol was almost negligible. While the solubility experiment of polyaniline Sn(IV) phosphate (Table 4) showed that the material has reasonable good chemical stability as the results indicated that the material was resistant to solutions of different acid, bases, organic solvents, salts *etc.* The chemical dissolution in DMW, alkaline media, CH_3COONa, NH_4NO_3, was almost negligible. The chemical stability of both the composite cation-exchangers may be due to the presence of binding polymer, which can prevent the dissolution of heteropolyacids sols or leaching of any constituent element into the solution.

The physico-chemical properties of these two composite materials (S-5 and T-7) were determined using some instrumental techniques, such as SEM, FTIR, and simultaneous TGA/DTA, powder XRD, UV-VIS spectrophotometry, AAS, elemental analyses, etc. The SEM pictures of both the materials showed the difference in surface morphology of organic polymer, inorganic precipitate and composite materials. Which indicated the change of morphology after binding of polypyrrole with Th(IV) phosphate and polyaniline with Sn(IV) phosphate. FTIR spectra of the composites recorded by KBr method revealed the presence of

Table 3

Chemical stability of polypyrrole Th(IV) phosphate in various solvents

Solvent used (20 ml)	Amount dissolved (mg/20 ml)	
	Th(IV)	Phosphorus
DMW	0.00	0.25
1 M HCl	0.12	1.88
2 M HCl	0.35	2.62
4 M HCl	Completely dissolved	
1 M HNO_3	0.27	1.55
2 M HNO_3	0.69	3.12
4 M HNO_3	Completely dissolved	
0.5 M H_2SO_4	0.93	7.54
2 M H_2SO_4	Completely dissolved	
1 M $HClO_4$	0.23	2.02
2 M $HClO_4$	0.62	3.55
4 M $HClO_4$	Completely dissolved	
0.1 M KOH	0.07	1.04
0.1 M NaOH	0.06	0.84
1 M NH_4OH	0.04	1.50
1 M $NaNO_3$	0.00	0.38
10% Dimethylsulphoxide (DMSO)	0.00	0.21
Acetone	0.00	0.22
n-Butyl alcohol	0.01	0.45

Table 4

Chemical stability of polyaniline Sn(IV) phosphate in various solvents

Solvent used (20 ml)	Amount dissolved (mg/20 ml)	
	Sn(IV)	Phosphorus
DMW	0.00	0.150
1 M HCl	0.04	0.965
2 M HCl	0.04	1.542
4 M HCl	0.04	1.672
1 M HNO_3	0.04	0.930
2 M HNO_3	0.04	1.333
4 M HNO_3	0.34	1.546
1 M H_2SO_4	0.05	0.863
2 M H_2SO_4	0.05	0.425
4 M H_2SO_4	0.06	0.841
1 M Formic acid	0.06	1.942
1 M Citric acid	0.05	0.756
1 M CH_3COOH	0.05	1.347
0.1 M KOH	0.00	1.020
0.1 M NaOH	0.00	0.783
1 M CH_3COONa	0.00	0.312
1 M NH_4NO_3	0.02	0.985
10% Dimethylsulphoxide (DMSO)	0.11	1.860
Acetone	0.05	0.512
n-Butyl alcohol	0.07	1.423

external water molecules in addition to the –OH groups and metal oxides present internally in the materials, ionic phosphate groups as well as stretching vibrations of C-N which also indicates that the materials contain considerable amount of pyrrole and aniline, respectively.

The TGA-DTA analyses of the composites showed the weight loss due to gel water, water of crystallization, coordination water and condensation of hydroxyl groups, etc which indicated the changes taking place in the composite lattice within the temperature range of 50-200 °C. Complete decompositions of the organic parts were also evident from the TGA curves. Smooth horizontal sections in the TGA curves represent the complete formation of the oxide forms of the materials. These transformations have also been supported by differential thermal analysis (DTA).

The X-ray powder diffraction pattern of polypyrrole Th(IV) phosphate cation-exchanger sample exhibited no peak in the spectrum that suggesting an amorphous nature of the composite material, while X-ray diffraction pattern of the polyaniline Sn(IV) phosphate composite cation-exchanger showed very small peaks of 2θ values. The analysis of these small signal peaks support towards its semi-crystalline nature.

The chemical compositions of the materials were obtained from the studies of UV-VIS spectrophotometry, AAS and elemental analyses. On the basis of chemical composition studies and various instrumental analyses, we can suggest the tentative formula of the composite materials: $\mathbf{[(ThO_2)(H_3PO_4)_2.(-C_4H_2NH-)_3].\mathit{n}H_2O}$ for polypyrrole Th(IV) phosphate and $\mathbf{[(SnO_2)(H_3PO_4)_3.(-C_6H_4NH-)].\mathit{n}H_2O}$ for polyaniline Sn(IV) phosphate.

Chapter – 3 entitled *"Studies on ion-exchange properties of polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate composite cation-exchangers"*. In this chapter ion-exchange properties of the materials were carried out such as ion-exchange capacity, effect of eluent concentration on the ion-exchange capacity, the elution behavior, pH-titration, thermal effect on ion-exchange capacity, distribution studies for metal ions and ion-exchange kinetics of various metal ions. The ion-exchange capacities of sample S-5 and sample T-7 were determined for some alkali and alkaline earth metal ions. Both the composite cation-exchange materials possessed a better Na^+ ion-exchange capacity (1.56 meq g^{-1}) for polypyrrole Th(IV) phosphate as compared to inorganic precipitate of fibrous type Th(IV) phosphate (0.72 meq g^{-1}) and (1.96 meq g^{-1}) for polyaniline Sn(IV) phosphate as compared to Sn(IV) phosphate (1.12 meq g^{-1}). The ion-exchange capacity was also found higher in comparison of some other similar materials prepared earlier. The ion-exchange capacity of these composite cation-exchangers for alkali metal ions and alkaline earth metal ions increased according to the decrease in their hydrated ionic radii as evident from Table 5.

The column elution experiments indicated that the minimum molar concentration of $NaNO_3$ as eluent for sample S-5 and sample T-7 was found 1 M for maximum release of H^+ ions from 1 g of the cation-exchanger column as shown in Fig. 1 and Fig. 2. It was observed from the elution behavior that the exchange is quite fast at the beginning as all the exchangeable H^+ ions for both the ion-exchangers sample S-5 and T-7 were eluted out in the first 150 ml of the

Table 5

Ion-exchange capacity of various exchanging ions on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers

Exchanging ions	pH of the metal solutions	Ionic radii (A°)	Hydrated ionic radii (A°)	Ion-exchange capacity (meq dry g^{-1})			
				Polypyrrole Th(IV) phosphate (S-5)		Polyaniline Sn(IV) phosphate (T-7)	
				H^+ -liberation	H^+ -absorption	H^+ -liberation	H^+ -absorption
Li^+	6.7	0.68	3.40	1.05	1.00	1.43	1.41
Na^+	6.7	0.97	2.76	1.56	1.29	1.96	1.82
K^+	6.8	1.33	2.32	1.21	1.22	2.07	2.09
Mg^{2+}	6.5	0.78	7.00	1.15	1.17	2.05	2.03
Ca^{2+}	6.5	1.06	6.30	1.38	1.35	2.15	2.16
Sr^{2+}	6.3	1.27	-	1.89	1.85	2.26	2.29
Ba^{2+}	6.3	1.43	5.90	2.74	2.75	2.32	2.33

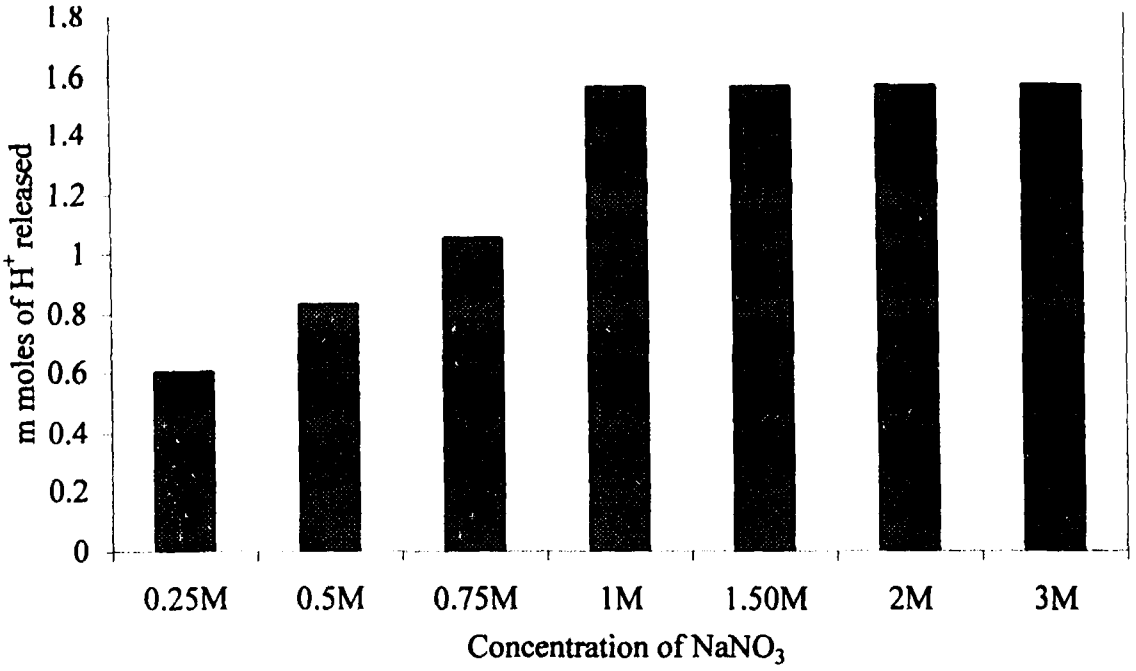

Fig. 1. Effect of eluent concentration on ion-exchange capacity of polypyrrole Th(IV) phosphate cation-exchanger.

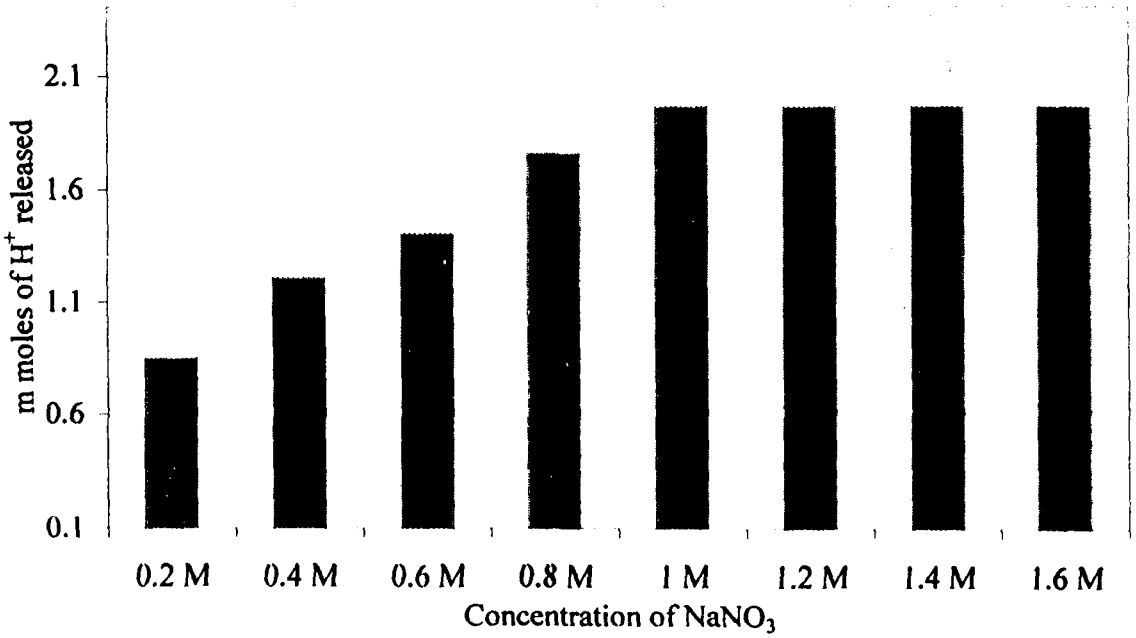

Fig. 2. Effect of eluent concentration on ion-exchange capacity of polyaniline Sn(IV) phosphate cation-exchanger.

effluent within 5 h. pH- titrations for LiOH/LiCl, NaOH/NaCl and KOH/KCl systems performed on these materials indicated bifunctional behavior of the materials. The composite materials appear to be strong cation-exchangers as indicated by a low pH (~ 1.5 for S-5 and ~2.0 for T-7) of the solutions when no OH^- ions were added to the system. The theoretical ion-exchange capacities for both the composite cation exchangers sample S-5 and T-7 was found to be ~2.5 meq g^{-1}. Both the composite cation-exchangers were found to possess higher thermal stability as polypyrrole Th(IV) phosphate sample (S-5) maintained about 69% of the initial mass by heating up to 400 °C and with respect to the ion-exchange capacity, this material was found stable up to 150 °C and it retained about 56% of the initial ion-exchange capacity by heating up to 350 °C (Table 6). While polyaniline Sn(IV) phosphate sample (T-7) maintained about 67% of the initial mass by heating up to 500 °C. However, with respect to ion-exchange capacity, this material was found stable up to 150 °C and it retained about 59% of the initial ion-exchange capacity by heating up to 350 °(Table 6).

The distribution (sorption) studies of different metal ions performed in different solvent systems showed that the distribution coefficients (K_d values) varied with the composition and nature of the contacting solvents. On the basis of distribution studies polypyrrole Th(IV) phosphate sample (S-5) and polyaniline Sn(IV) phosphate sample (T-7) cation-exchangers were found to be highly selective towards Pb(II) and Hg(II) respectively, which are the major polluting elements in the water.

Table 6

Effect of temperature on ion-exchange capacity of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers on heating time for one hour

Heating temperature (°C)	Polypyrrole Th(IV) phosphate (S-5)				Polyaniline Sn(IV) phosphate (T-7)			
	Appearance (color)	Weight loss (%)	Na^+ ion-exchange capacity (meq dry g^{-1})	% Retention of i.e.c.	Appearance (color)	Weight loss (%)	Na^+ ion-exchange capacity (meq dry g^{-1})	% Retention of i.e.c.
40	Blackish brown	-	1.56	100	Greenish	-	1.96	100
100	Blackish brown	9.34	1.56	100	Greenish	8.60	1.96	100
150	Blackish brown	12.15	1.56	100	Greenish	14.12	1.96	100
200	Blackish brown	13.46	1.32	84.61	Greenish	16.50	1.71	87.12
300	Black	19.26	0.96	61.54	Dark green	20.00	1.42	72.46
350	Black	25.07	0.87	55.77	Black	22.13	1.16	59.31
400	Black	30.08	0.45	28.85	Blackish brown	23.42	0.77	39.29
500	Light gray	39.42	0.33	21.15	Slightly white	32.64	0.53	26.94
600	Light gray	43.91	0.22	14.10	White	34.00	0.22	11.02

The ion-exchange kinetic studies carried out on composite cation-exchangers indicated that the ion-exchange process taking place on the surface of the materials is a particle diffusion controlled phenomenon and it also revealed that equilibrium is attained faster at a higher temperature. The values of the self-diffusion coefficients, energies and entropies of activation were obtained on the basis of non linear Nernst-Plank equations that should be applicable for a particle diffusion-controlled ion-exchange with some additional assumptions. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange process.

Chapter – 4 entitled ***"Electrical conductivity measurement studies of "organic-inorganic" composites: polypyrrole Thorium(IV) phosphate & polyaniline Sn(IV) phosphate"*** deals with the electrical conducting behavior of polypyrrole Thorium(IV) phosphate & polyaniline Sn(IV) phosphate composite cation-exchange materials. Various samples of both the composites were prepared using the method described in Chapter – 2 by mixing different concentrations of pyrrole (approximately 3.33 to 40%; vol.%) and aniline (2 to 20% (vol.%) monomers into fixed volume of inorganic precipitates of Th(IV) phosphate and Sn(IV) phosphate, respectively as given in Table 7 and Table 8. Among these, sample PT-10 and PS-5 (Table 7 and Table 8) were selected for detail electrical conductivity studies.

The electrical conductivity was measured using 4-probe-in-line dc electrical conductivity measuring technique for semiconductors that is more satisfactory than two-probe method. On examination, it was observed that the electrical

Table 7

Preparation of various samples of polypyrrole Th(IV) phosphate composite material with fixed volume of inorganic precipitates

Samples	Mixing volume ratios (v/v)				Appearance of the beads after drying
	0.1 M $Th(NO_3)_4.5H_2O$ in 1 M HNO_3	H_3PO_4	Pyrrole in toluene (Vol. %)	0.1 M $FeCl_3$	
PT-1	5	2 (2 M)	0.30 (3.33%)	2	Blackish granular
PT-2	5	2 (2 M)	0.30 (6.66 %)	2	Blackish granular
PT-3	5	2 (2 M)	0.03 (10 %)	2	Blackish granular
PT-4	5	2 (2 M)	0.30 (13.33 %)	2	Blackish granular
PT-5	5	2 (2 M)	0.30 (16.66 %)	2	Blackish granular
PT -6	5	2 (2 M)	0.30 (20 %)	2	Blackish granular
PT-7	5	2 (2 M)	0.30 (23.33 %)	2	Blackish granular
PT-8	5	2 (2 M)	0.30 (26.66 %)	2	Blackish granular
PT-9	5	2 (2 M)	0.30 (30 %)	2	Blackish granular
PT-10	5	2 (2 M)	0.30 (33.33 %)	2	Blackish granular
PT-11	5	2 (2 M)	0.30 (36.66 %)	2	Blackish granular
PT-12	5	2 (2 M)	0.30 (40 %)	2	Blackish granular

Table 8

Preparation of various samples of polyaniline Sn(IV) phosphate composite material with fixed volume of inorganic precipitates

Samples	Mixing volume ratios (v/v)					Appearance of the yield after drying
	0.1 M $SnCl_4.5H_2O$ in 4 M HCl	0.1 M Na_2HPO_4 in DMW	pH of the inorganic precipitate	0.1 M $K_2S_2O_8$ in 1 M HCl	Aniline in 1 M HCl (vol.%)	
PS-1	2	3	1.0	1	1 (2%)	Greenish granular
PS-2	2	3	1.0	1	1 (4%)	Greenish granular
PS-3	2	3	1.0	1	1 (6%)	Greenish granular
PS-4	2	3	1.0	1	1 (8%)	Greenish granular
PS-5	2	3	1.0	1	1 (10%)	Greenish granular
PS-6	2	3	1.0	1	1 (12%)	Greenish granular
PS-7	2	3	1.0	1	1 (14%)	Greenish granular
PS-8	2	3	1.0	1	1 (16%)	Greenish granular
PS-9	2	3	1.0	1	1 (18%)	Greenish granular
PS-10	2	3	1.0	1	1 (20%)	Greenish granular

conductivity of the composite samples increase with the increase in temperature and the values lie in the order of 10^{-6} to 10^{-4} S cm^{-1}, for polypyrrole Th(IV) phosphate and 10^{-5}-10^{-3} S cm^{-1} for polyaniline Sn(IV) phosphate *i.e.*, in the semiconductor region. It was also observed that the composite samples followed the Arrhenius-type equation for the dependence of electrical conductivity with temperature similar to other semiconductors as shown in Fig. 3 and Fig. 4.

The dependence of the electrical conductivity through the bi-phasic systems (polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composites; prepared with different concentrations of pyrrole and aniline monomers) on the concentration of conducting phases (i.e. polypyrrole and polyaniline, respectively) was examined (Table 9 and Table 10). A slight increase in electrical conductivity for these composites is followed at a certain pyrrole and aniline concentration by a sudden jump, which is again followed by moderate increase. At about 23.33% pyrrole and 8% aniline concentration (critical concentration of conducting phase), the sharp rise in electrical conductivity is observed that could possibly be explained on the basis of percolation theory. Thus, we can say that main factor that made the composites electrically conducting is the presence of polypyrrole or polyaniline in sufficient amount. It was also observed that the ambient temperature conductivities of the composites for some concentrations of pyrrole and aniline monomers are greater than that of polypyrrole (prepared as 33.33% pyrrole in toluene) and polyaniline (prepared as 10% aniline in 1 M HCl) as shown in Table 9 and Table 10.

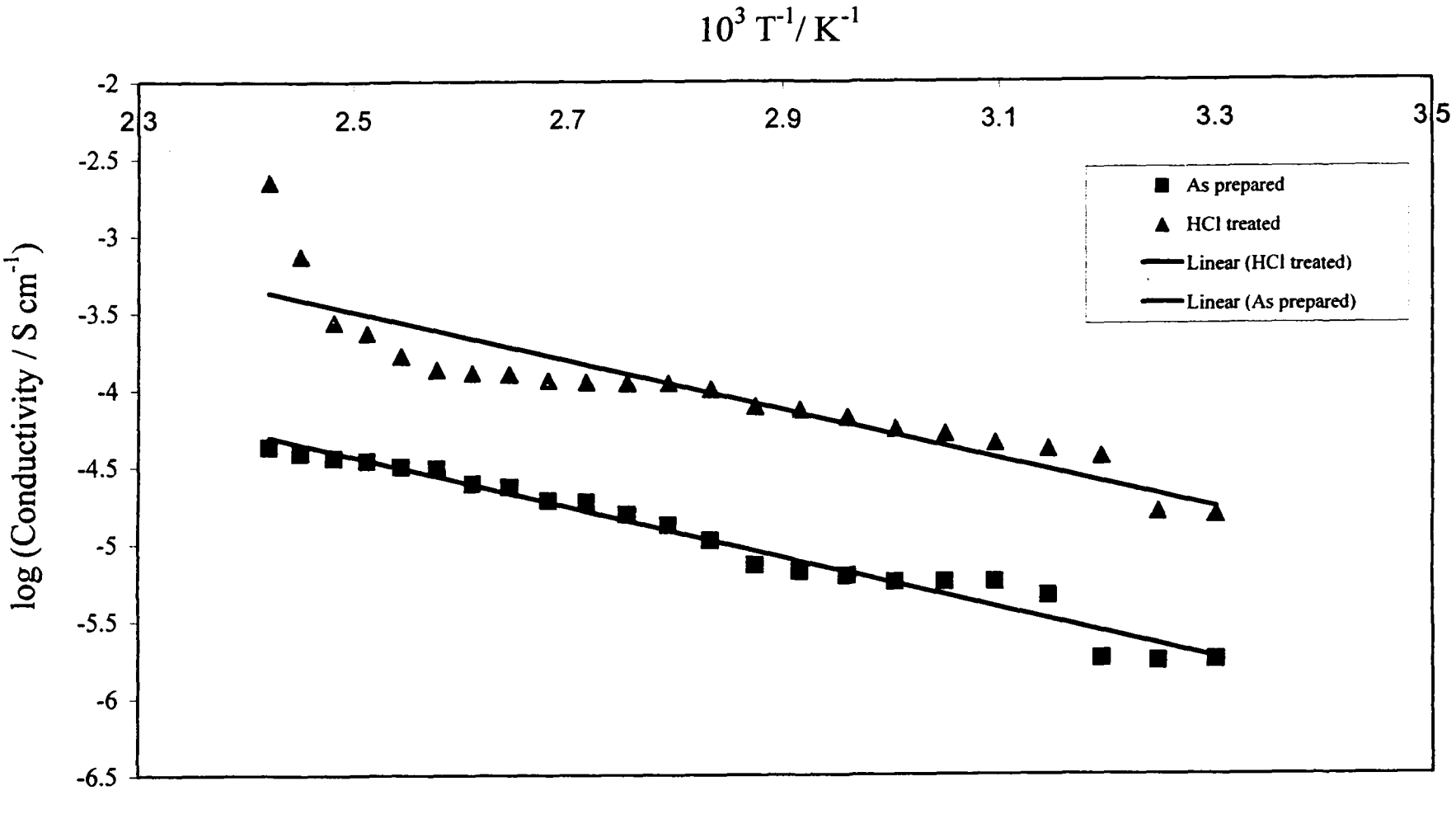

Fig. 3. Arrhenius plots for polypyrrole Th(IV) phosphate composite material (as prepared and HCl treated).

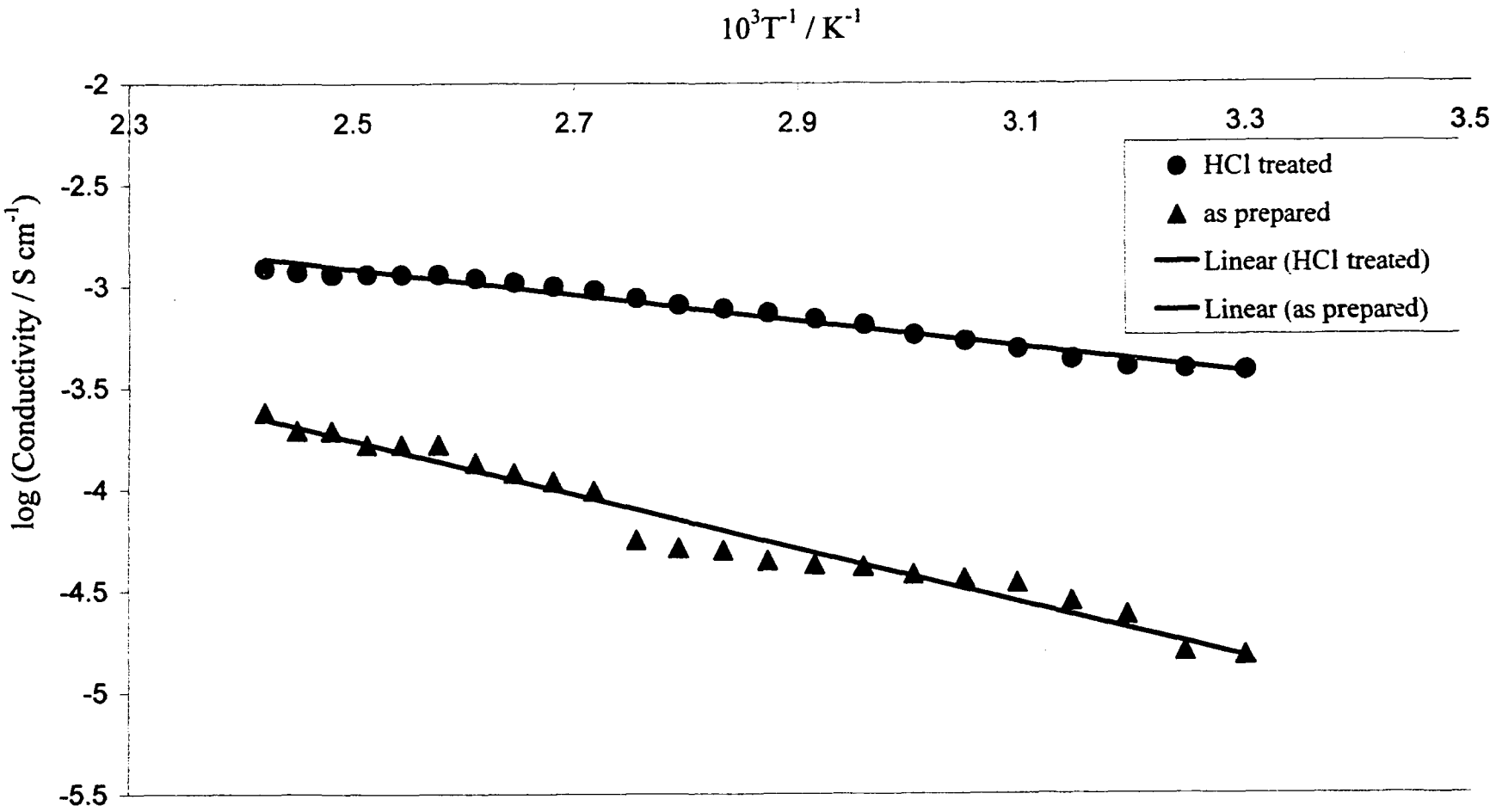

Fig. 4. Arrhenius plots for polyaniline Sn(IV) phosphate composite material (as prepared and HCl treated).

Table 9

Values of dc electrical conductivity for the polypyrrole and polypyrrole Th(IV) phosphate composites with different concentrations of pyrrole monomer

Sample No.	Polypyrrole (prepared with 33.33% pyrrole in toluene)	Polypyrrole Th(IV) phosphate	
	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)	Pyrrole monomer concentration (vol. %)	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)
1	3.28×10^{-5}	3.33	4.13×10^{-8}
2		6.66	5.19×10^{-8}
3		10	2.82×10^{-8}
4		13.33	3.84×10^{-8}
5		16.66	5.92×10^{-8}
6		20	6.15×10^{-8}
7		23.33	2.53×10^{-5}
8		26.66	3.47×10^{-5}
9		30	3.54×10^{-5}
10		33.33	3.82×10^{-4}
11		36.66	4.90×10^{-4}
12		40	5.16×10^{-4}

Table 10

Values of dc electrical conductivity for the polyaniline and polyaniline Sn(IV) phosphate composite with different concentrations of aniline monomer

Sample No.	Polyaniline (prepared with 10% aniline in 1 M HCl)	Polyaniline Sn(IV) phosphate	
	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)	Aniline monomer concentration (vol. %)	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)
1	9.12×10^{-4}	2	3.20×10^{-6}
2		4	5.82×10^{-6}
3		6	9.46×10^{-5}
4		8	2.54×10^{-4}
5		10	5.23×10^{-3}
6		12	6.48×10^{-3}
7		14	6.93×10^{-3}
8		16	8.01×10^{-3}
9		18	5.20×10^{-3}
10		20	3.12×10^{-3}

The electrical conductivity measured with respect to the time of accelerated ageing of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite materials (PT-10 and PS-5) showed that the electrical conductivity for both the composite materials is quite stable at 50, 70, 90 and 110 °C that supports the fact that the dc electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150 °C that may be attributed to the loss of dopant and the chemical reaction of dopant with the material.

The stability of both HCl treated composite materials (PT-10 and PS-5) in terms of electrical conductivity retention monitored for 5 cycles for both the composite materials showed that each plot followed the Arrhenius equation for its temperature dependence similar to other semiconductors. There was minor difference in their electrical conductivity even after repeating the experiment for five times that showed the good stability of the materials during heating-cooling cycles under severe oxidizing conditions up to 200 °C. These composites were also observed to be stable materials, *i.e.* the room temperature conductivities are negligibly affected by short-term exposure to laboratory. The composites are environmentally stable with respect to their physical properties and no visible deterioration could be traced in the pellets even after 250 days of their preparation.

Chapter – 5 entitled ***"Preparation and characterization of ion- exchange membranes and ion-selective electrodes based on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate"*** deals the preparation and characterization of the ion-

exchanger membranes and ion-selective membrane electrodes using the composite cation-exchange materials as an electroactive components. Polypyrrole Th(IV) phosphate cation-exchanger membrane was prepared by mixing 100 mg fine powder of sample S-5 thoroughly with Araldite (Ciba-Geigy, India Ltd.) (100 mg) in 1:1 (*w/w*) ratio to make a homogeneous paste, which was then spread between the folds of Whatman's filter paper No. 42. Glass plates were kept below and above the filter paper folds as support. The phase of the exchanger and Araldite was kept under pressure of 2 Kg. cm^2 for 24 h and left to dry. A uniform and thin membrane having 0.42 mm thickness was obtained. Polyaniline Sn(IV) phosphate cation-exchanger membrane was prepared by mixing fine powder of sample T-7 (200 mg) thoroughly with poly(vinyl chloride) solution (200 mg PVC dissolve in 10 ml THF) and finally 10 drops of a plasticizer dioctylphthalate was mixed into the solution. The resulting solution was carefully cast on a glass slide plate and left for slow evaporation to obtain a thin membrane. Finally, a thin master membrane of 0.36 mm thickness was obtained. The physico-chemical properties of the membranes *viz.*, thickness, water content, porosity, swelling etc. were also determined. Since both the composite cation-exchangers polypyrrole Th(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7) having selectivity towards Pb(II) and Hg(II), respectively; the membranes were equilibrated with the solutions of selected ions of Pb(II) and Hg(II), and then taken for potentiometric studies. Polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composites membranes were utilized to fabricate its ion-selective membrane electrodes with satisfactory detection limits (5×10^{-6} M and 1×10^{-6} M with close

Nernstian slopes), high working pH ranges (between 3.0-8.5 and 4.0-9.0), quick responses (between 35 and 40 sec.) and enough lifetimes (between 3 months), respectively. The membrane electrodes were also used for for the selective determination of heavy metal ions (*i.e.* Pb^{2+} and Hg^{2+} that causes hazardous pollution in the environment) in synthetic samples as well as real samples.

In order to assess the selectivity of the membrane electrodes, the effect of a number of interfering ions (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+} etc.) on the membrane potentials were evaluated by Fixed Interference Method. The results of potentiometric selectivity coefficients revealed that all other foreign metal ions interfere to a very little extent with the primary ion (Pb^{2+} and Hg^{2+}) response. Thus, the electrodes are selective for Pb(II) and Hg(II) in presence of interfering cations.

Chapter – 6 entitled "***Analytical applications of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers in separation of metal ions, determination of Pb(II) & Hg(II) from samples of waste water using ion-selective electrodes and adsorption of pesticides***" deals with the various analytical and environmental applications of the proposed composite materials used as cation-exchangers, adsorbents and ion-selective membrane electrodes. These composite materials were used as cation-exchangers for the selective separation of metal ions Fig. 5 and Fig. 6 and for determination preconcentration of toxic heavy metal ions Pb^{2+} and Hg^{2+} from other metal ions in aqueous solutions. It is evident from the thermodynamic study for the adsorption behavior of trichloroacetic acid and

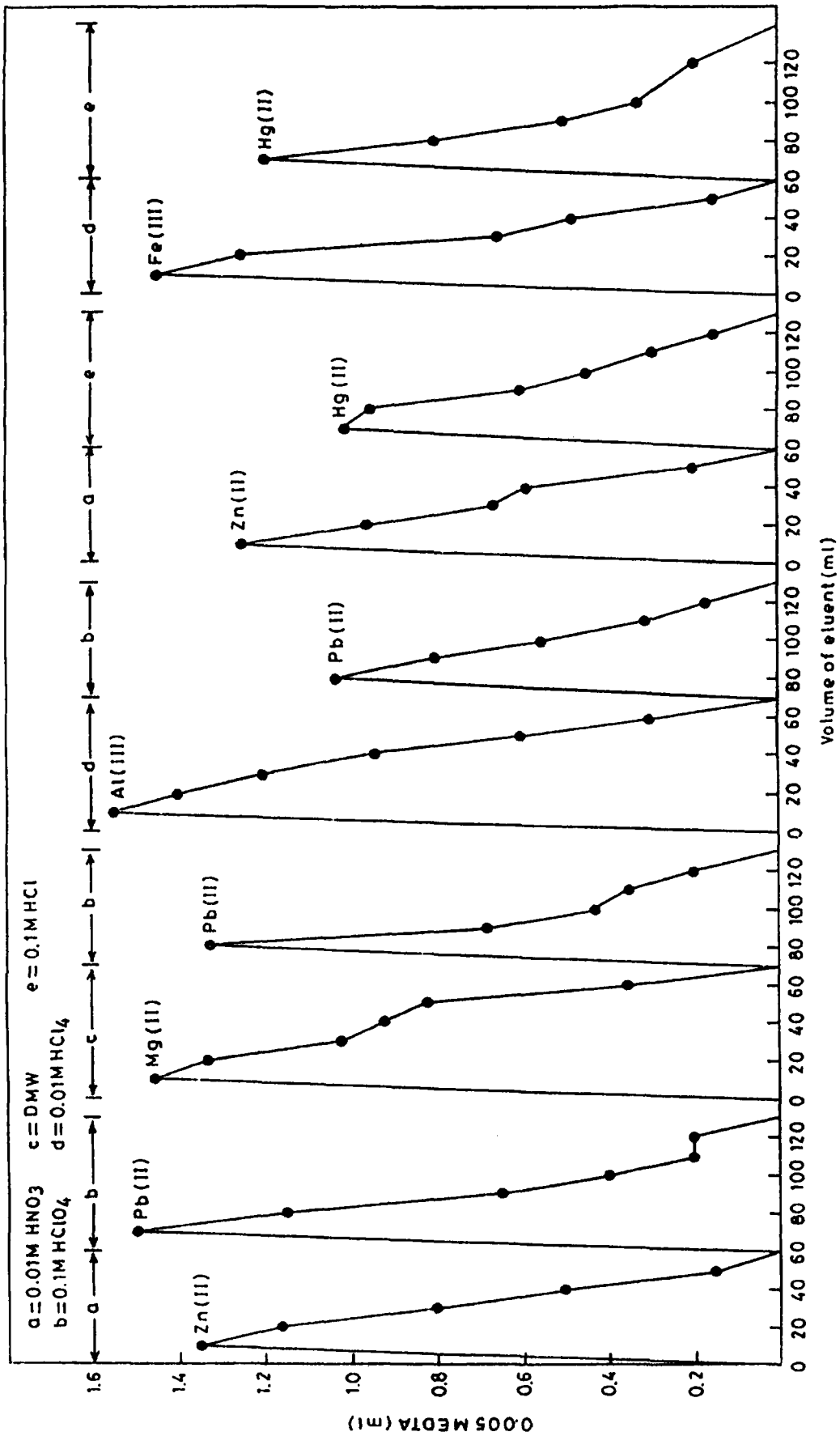

Fig. 5. Some binary separation of metal ions achieved on polypyrrole Th(IV) phosphate columns.

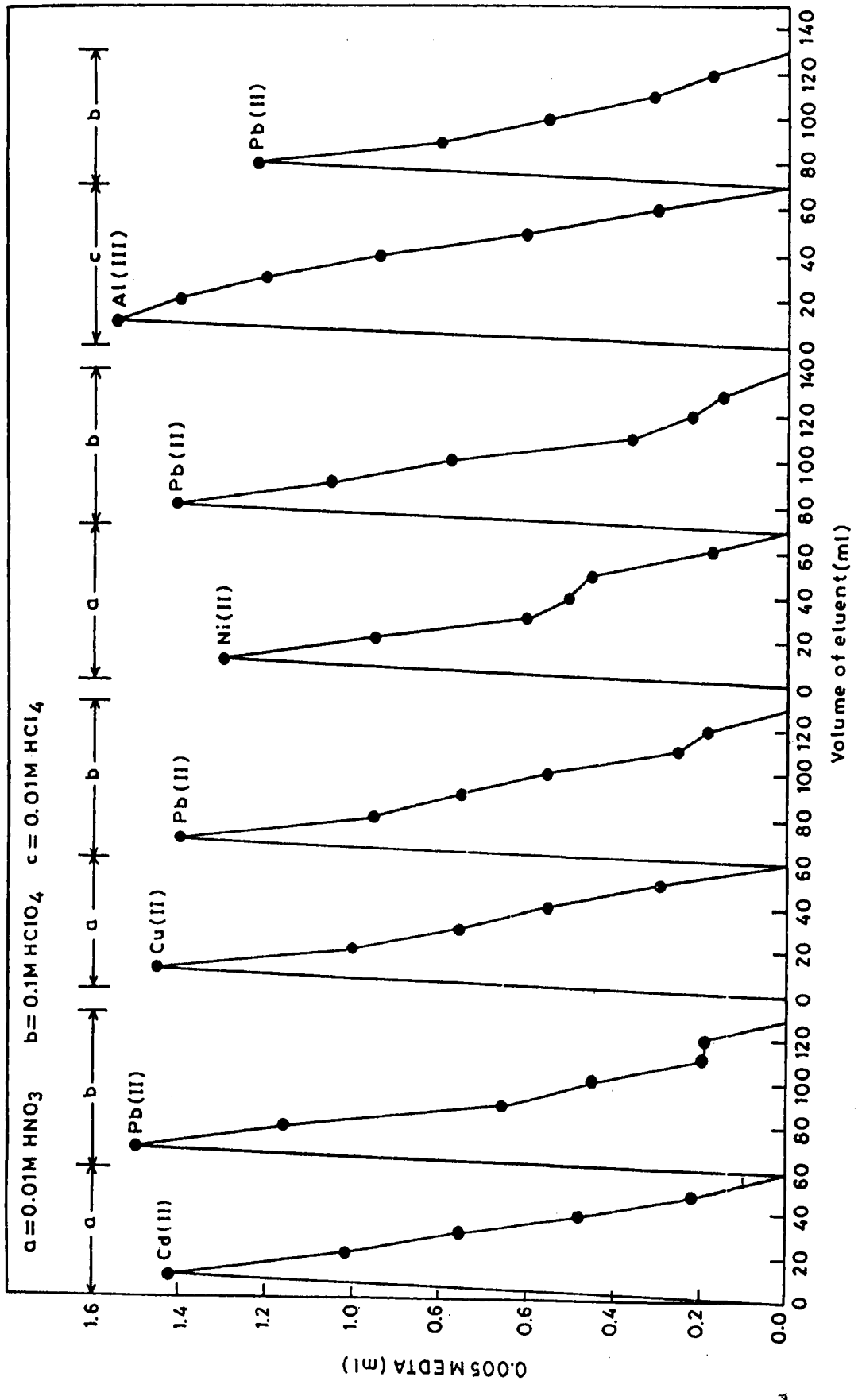

Fig. 5. Continued.

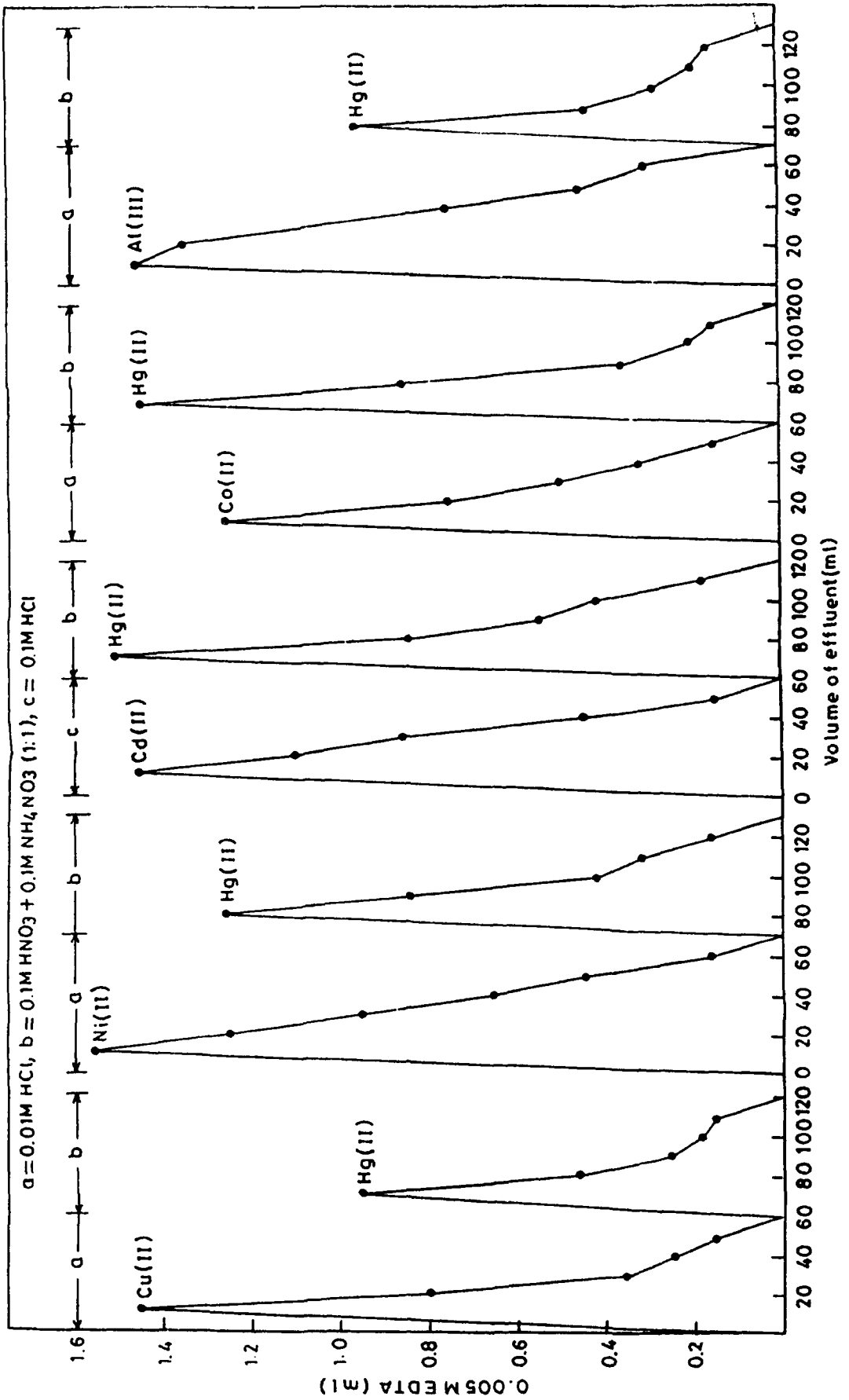

Fig. 6. Some binary separation of metal ions achieved on polyaniline Sn(IV) phosphate columns.

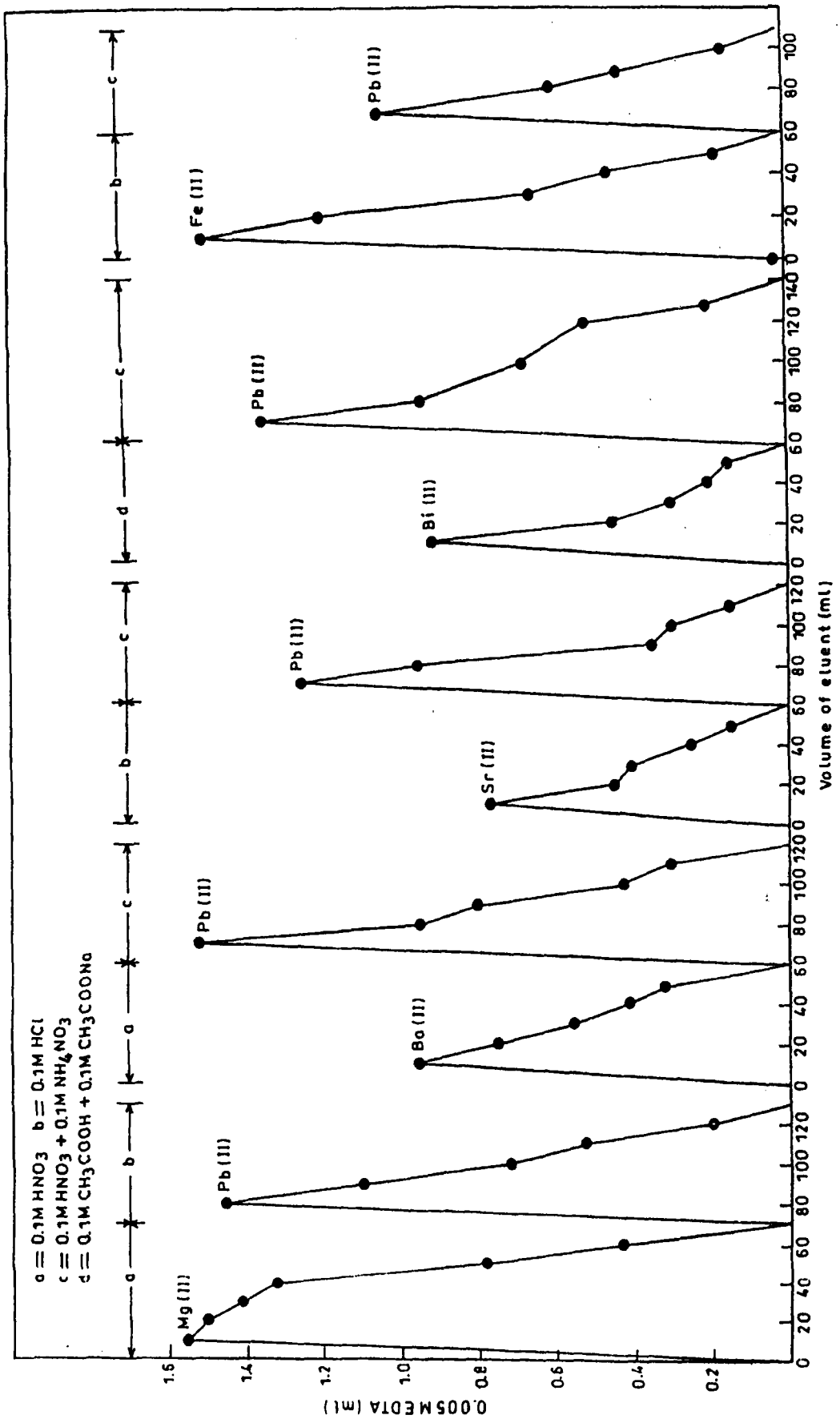

Fig. 6. Continued.

mancozeb pesticides on the surface of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate, respectively that the composite materials can be used as good adsorbents of pesticides to decrease the pollution load in the environment. The analytical applications of the membrane electrodes proved to be useful for the direct determination of Pb(II) and Hg(II) in the drain waters collected from Department of Chemistry and Department of Applied Chemistry, Aligarh Muslim University, Aligarh, (India) respectively. The concentration of lead and mercury in the sample was 10^{-2} and 10^{-3} M, respectively. The reproducibility of the results was checked to three times. The practical utility of the proposed membrane sensors assembly was also tested by its use as an indicator electrode in the potentiometric titration of Pb(II) and Hg(II) with EDTA.

In conclusion, we can say that in comparison compared with other ion-exchange materials of this class 'organic-inorganic' composite materials offer more advantages. A number of analytical applications of these materials such as separation of metal ions, determination of toxic heavy metals from waste water, in making ion-selective membrane electrodes and semi-conducting properties would make these materials important for materials as well as environmental scientists.

Suggestions for Future Work

The research work done in this thesis may be continued for the development of the materials of desirable properties by the new researchers of this discipline in the following directions-

- To develop simple selective and economical "organic-inorganic" composite

ion-exchange materials having selectivity towards heavy toxic metal ions and especially for radioactive elements coming from a high temperature radioactive waste streams to decrease the pollution load of the environment.

- To develop fibrous type composite ion-exchangers of recent origin having capability for obtaining in different forms such as conveyer belts, non-woven materials, staples, nets and cloths *etc.* These open new and novel possibilities, of using these materials in various industrial applications and in environmental analysis.
- To study in detail, the SEM (Scanning Electron Microscopy) analysis of the inorganic, organic as well as composite cation-exchanger in terms of surface morphology, pore size, *etc.*
- To develop electrically conducting nano-composite materials with higher electrical conductivity for their use in various electronic and photonic systems.
- To more studies of electrical behavior of electrically conducting "organic-inorganic" composite ion-exchange materials.
- The dc electrical conductivity of the composites may also be utilized as electrochemical sensor to evaluate toxic gases, volatile organic compounds and humidity sensing characteristics of these composites.
- Furthermore, to study in detail, the electrically conducting composite ion-exchange materials used as electrochemically switchable ion-exchangers for water treatment; especially for water softening.
- Efforts will be made to use these composites as adsorbents for air (*i.e.* gas separations) by controlling their electrical conductivity.

- A detailed study of composite ion-exchangers used as catalysts for reaction of gases and of liquids or solutes.
- Chromatographic and thin layer, separation, identification and determination of pharmaceuticals and related drugs in drugs formulations and biological samples.
- To develop ion-selective electrodes for a number of heavy toxic elements with detection limits down to parts-per-million levels 10^{-10} M, which is possible by studying the underlying chemical principles and modifying the nature of electroactive materials.

PREPARATION AND PROPERTIES OF SOME ORGANIC-INORGANIC ION-EXCHANGE MATERIALS

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

APPLIED CHEMISTRY

BY

INAMUDDIN

(M. Phil. Applied Chemistry)

UNDER THE SUPERVISION OF

DR. ASIF ALI KHAN

DEPARTMENT OF APPLIED CHEMISTRY
FACULTY OF ENGINEERING & TECHNOLOGY
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CERTIFICATE

This is to certify that the thesis entitled *"Preparation and properties of some organic-inorganic ion-exchange materials"* which is being submitted by *Mr. Inamuddin* for the award of the degree of Doctor of Philosophy in Applied Chemistry to the Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, India is entirely based on the experimental work carried out by him under my supervision. The work reported in this thesis embodies the work of the candidate himself and is original one, has not been submitted to any other University or Institution for the award of any degree or diploma.

Dated: 27th oct 2006

(ASIF ALI KHAN)

Dedication

This thesis is dedicated to

My

Adorable Parents,

Loving Nephew

Abdussubhan

And

Niece Sofia Ghayas

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Inamuddin

(Inamuddin)

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List of Publications

1. Electrical conductivity and ion-exchange kinetic studies of a crystalline type 'organic-inorganic' cation-exchange material: polypyrrole/polyantimonic acid composite system, (Sb_2O_5) $(-C_4H_2NH-)$. nH_2O

   Asif Ali Khan*, M.Mezbaul Alam Inamuddin, Faiz Mohammad, Journal of Electroanalytical Chemistry 572 (2004) 67-78.

2. Preparation, characterization and analytical applications of a new and novel electrically conducting fibrous type polymeric-inorganic composite material: polypyrrole Th(IV) phosphate used as a cation-exchanger and Pb(II) ion-selective membrane electrode

   Asif Ali Khan*, Inamuddin, M.Mezbaul Alam, Materials Research Bulletin 40 (2005) 289-305.

3. Determination and separation of Pb^{2+} from aqueous solutions using a fibrous type organic-inorganic hybrid cation-exchange material: polypyrrole Thorium(IV) phosphate

   Asif Ali Khan*, Inamuddin, M. Mezbaul Alam, Reactive and Functional Polymers 63 (2005) 119-133.

   This paper was selected for the award of top 25 best research articles by the publisher.

4. Preparation, physico-chemical characterization, analytical applications and electrical conductivity measurement studies of an 'organic-inorganic' composite cation-exchanger: polyaniline Sn(IV) phosphate

   Asif Ali Khan*, Inamuddin, Reactive and Functional Polymers (2006) in press.

5. Applications of Hg(II) sensitive polyaniline Sn(IV) phosphate composite cation-

exchange material in determination of Hg^{2+} from aqueous solutions and in making ion-selective membrane electrode

Asif Ali Khan*, Inamuddin, Sensors and Actuators B: Chemical (2006) in press.

6. Cation-exchange kinetics and electrical conductivity studies of an 'organic-inorganic' composite cation-exchanger: polypyrrole Th(IV) phosphate

   Asif Ali Khan*, Inamuddin, Journal of Applied Polymer Science (2006) in press.

7. Synthesis, characterization and ion-exchange properties of a new and novel 'organic-inorganic' hybrid cation-exchanger: Nylon-6,6, Zr(IV) phosphate

   Inamuddin, Shakeel A. Khan, Weqar A. Siddiqui[a], and Asif Ali Khan, Talanta (2006) in press.

8. Some physicochemical properties of unsaturated polyester resins derived from poly(ethylene terephthalate) waste soft drinking bottles

   Hussain Abbas, Fareed Mahdi, Inamuddin, and Asif Ali Khan* (Submitted after revision).

9. Cation-exchange kinetics on ployaniline Sn(IV) phosphate cation-exchanger for various metal ions

   Asif Ali Khan*, Inamuddin, Indian Journal Of Chemical Technology, (COMMUNICATED).

10. Organic-inorganic composite cation-exchanger: poly-o-toluidine Zr(1V) phosphate based ion-selective membrane electrode for the potentiometeric determination of mercury

    Asif Ali Khan*, Inamuddin and Tabassum Akhtar, Sensors and Actuators B: Chemical (COMMUNICATED).

11. Preparation and Characterization of a new organic-inorganic nano-composite poly-o-toluidine Th(IV) phosphate, its application as cation-exchanger and in making ion-selective membrane electrode

Asif Ali Khan*, Anish Khan and Inamuddin, Talanta (COMMUNICATED).

12. Thermodynamic studies for the adsorption of mancozeb pesticide on the surface of the. polyaniline Sn(IV) phosphate organic-inorganic composite cation-exchanger

Asif Ali Khan*, Inamuddin, Indian J. Chem. Tech. (COMMUNICATED).

13. Physiochemical and Structural Properties of Polymer Mortar Derived From Glycolysis of poly(ethylene terephthalate) Waste using Ethylene Glycol

Husain Abbas[a] Asif Ali Khan[b], Fareed Mahdi[c*], and Inamuddin (COMMUNICATED).

14. Synthesis and characterization of poly-o-toluidine Zr(1V) phosphate Hg(II) selective composite cation-exchanger

Asif Ali Khan*, Inamuddin and Tabassum Akhtar, J. Hazard. Mat. (COMMUNICATED).

LIST OF PAPAERS PRESENTED IN SEMINARS AND ABSTRACT PUBLISHED

1. Third International Conference on Surface Science and Catalysis; December 8-9, 2003, Ajmer, India.

   (Abstract Published and full-length paper presented)

2. A seminar on Environmental vision: retrospect and Prospect: February 28, 2004, Etawah, U.P. India.

   (Abstract Published and full-length paper presented)

3. International Activated Carbon Conference; September 25-26, 2003, Pittsburgh, Pennsylvania, U.S.A.

   (Abstract published)

4. Second International Symposium on the Separation and Characterization of Natural and Synthetic Macromolecules (SCM-2)", on February 2nd - 4th, 2005 in Amsterdam (The Netherlands).

   (Abstract accepted}

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CHAPTER 3

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General Introduction

Chapter 1

1.1. Composite Materials

Mankind has been aware of composite materials since several hundred years before Christ and has applied innovations to improve the quality of life. It is not clear as to how as understood the fact that mud bricks made sturdier houses if lined with straw, he used them to make building that lasted. Long Ancient Pharaohs made their slaves use bricks with straw to enhance the structural integrity of their buildings, which testifies to the wisdom of the dead civilization. Although, composites were known to mankind since prehistoric times, the concept and technology have undergone a sea change with better understanding of the basics like the bonding mechanism between the matrix and dispersoids, dispersoid size and distribution, morphological features etc. [1].

The term "composite materials" may, perhaps, be simply defined on the basis of the classical definition of a "composite material" as given in "Longman's dictionary" "something combining the typical or essential characteristics of individuals making up a group". This short statement grasps the very essence of this new material, which has recently emerged as a leading contender for numerous applications in the automotive, aerospace, electronic and wears industry [1].

1.1.1. Classification of composite materials

Many composite materials are composed of just two phases; one is termed the

matrix, which is continuous and surrounds the other phase, often called the dispersed phase. The properties of composites are a function of the properties of the constituent phases, their relative amounts, and the geometry of the dispersed phase (i.e., the shape of the particles and particle size, distribution, and orientation); these characteristics are represented in Fig. 1.1.

One simple scheme for the classification of composite materials [1,2,] is shown in Fig. 1.2, which consists of three main divisions– particle-reinforced (dispersed phase is equiaxed, i.e., particle dimensions are approximately the same in all directions), fiber-reinforced (dispersed phase has the geometry of a fiber) and structural composites (combinations of composites and homogeneous materials).

As noted in Fig. 1.2, large particle and dispersion-strengthened composites are the two sub-classifications of particle-reinforced composites. The distinction between these, is based upon reinforcement or strengthening mechanism. The term 'large' is used to indicate that particle –matrix interactions cannot be treated on the atomic or molecular level. Some polymeric materials to which fillers have been added are really large-particle composites. Again, the fillers modify or improve the properties of the material and/or replace some of the polymer volume with a less expensive material –the filler. In dispersion-strengthened composites, materials may be strengthened and hardened by the uniform dispersion of several volume percent of fine particles of a very hard and inert material. The dispersed phase may be metallic or nonmetallic; oxide materials are often used. Again, the strengthening mechanism involves interactions between the particles and dislocations within the matrix, as with

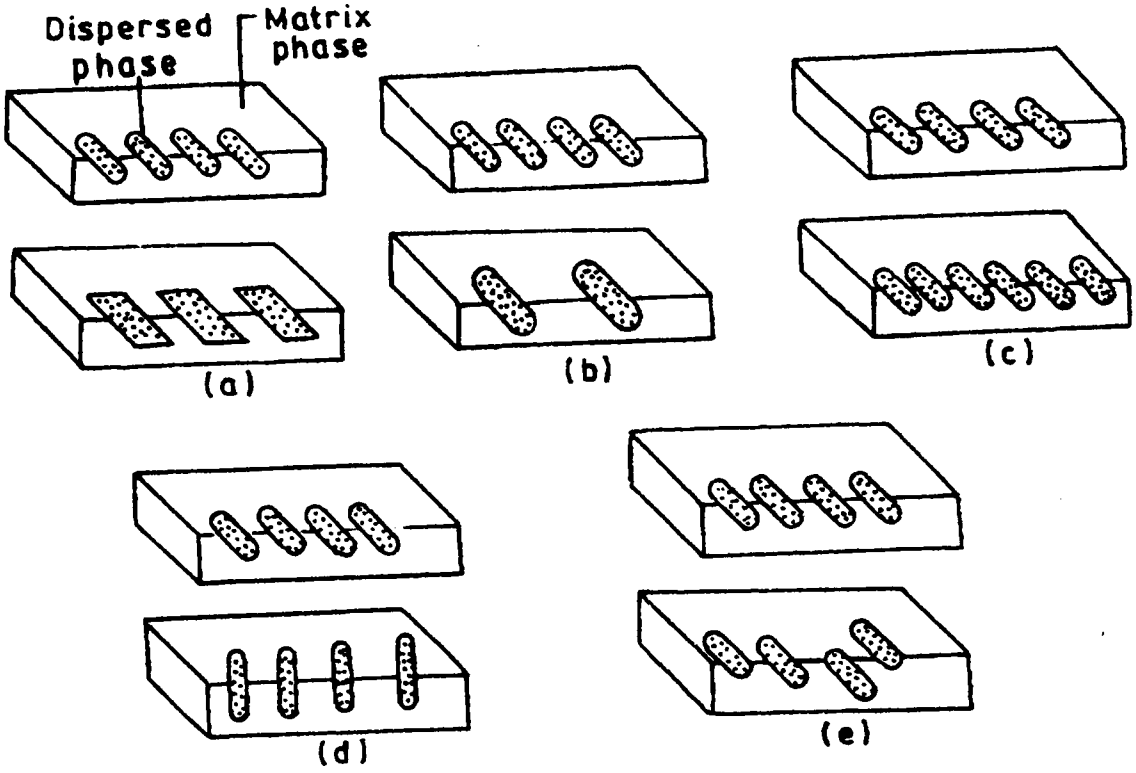


Fig. 1.1. Schematic representations of the various geometrical and spatial characteristics of particles of the dispersed phase (a. shape, b. size, c. concentration, d. orientation and e. distribution) that may influence the properties of composites.

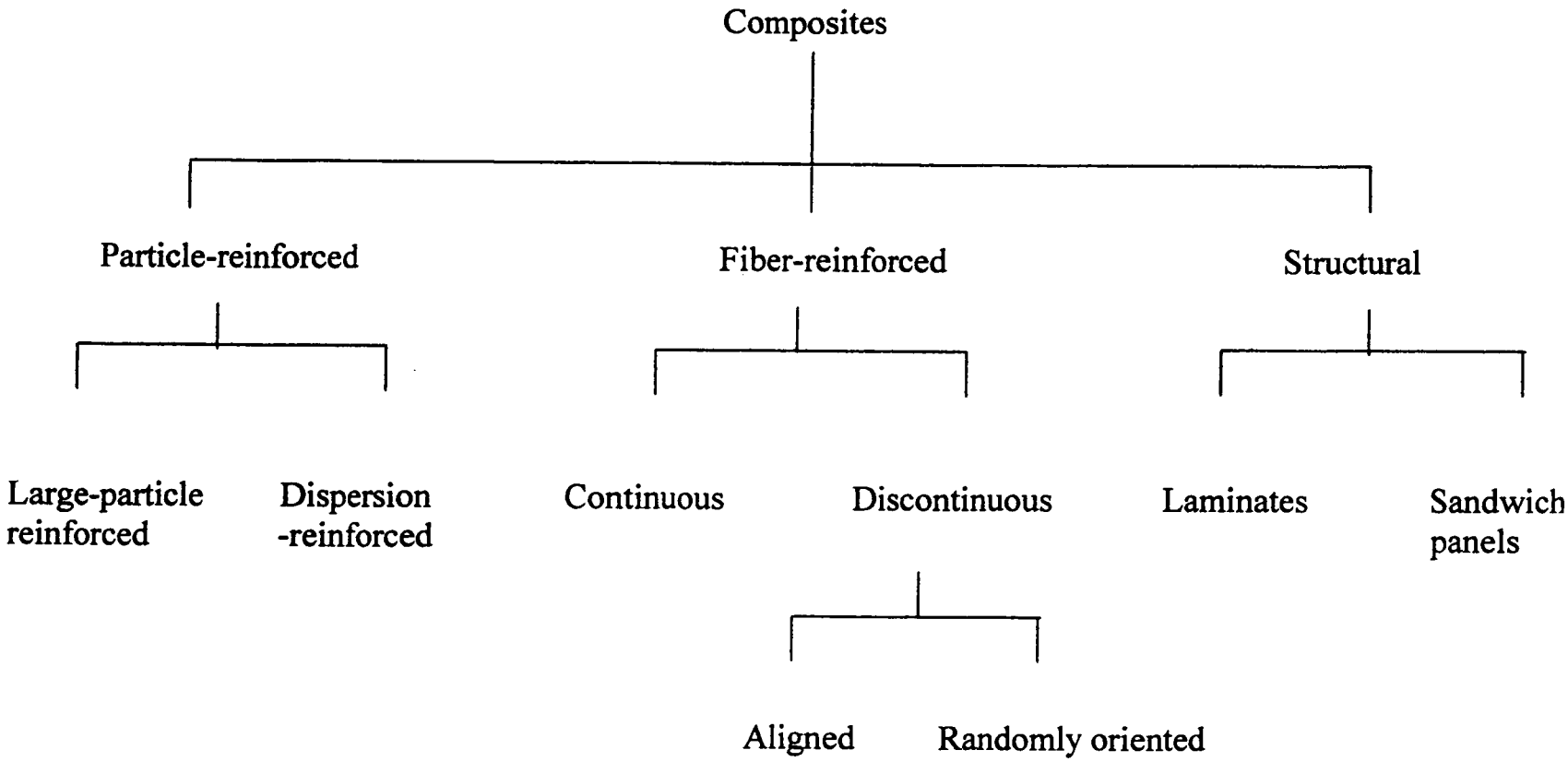


Fig. 1.2. Classification scheme for the various composite materials.

precipitation hardening; and the strengthening is retained at elevated temperatures and for extended time periods because the dispersed particles are chosen to be unreactive with the matrix phase.

Technologically, the most important composites are those in which the dispersed phase is in the form of a fiber. Design goals of fiber-reinforced composites (for those the potential for reinforcement efficiency is greatest) often include high strength and/or stiffness on a weight basis. These composites with exceptionally high specific strengths and moduli have been produced that utilize low-density fiber and matrix materials. As noted in Fig. 1.2, fiber-reinforced composites are sub-classified by fiber length. For short fiber composites, the fibers are too short to produce a significant improvement in strength. On the basis of diameter, fiber reinforcements are classified as whiskers, fibers, or wires. These types of composites are sometimes classified according to matrix type, viz. polymer-, metal-, and ceramic-matrix. Polymer-matrix are the most common, which may be reinforced with glass, carbon, and aramid fibers. Service temperatures are higher for metal-matrix composites, which also utilize a variety of fiber and whisker types. The objective of many polymer- and metal-matrix composites is a high strength and/or specific modulus, which require matrix materials having low densities. With ceramic-matrix composites, the design goal is increased fracture toughness. Other more advanced composites and promising engineering materials are carbon-carbon (carbon fibers embedded in a pyrolyzed carbon matrix) and the hybrids (containing at least two different fiber types).

A structural composite is normally composed of both homogeneous and heterogeneous composite materials, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Laminar composites (composed of two-dimensional sheets or panels that have a preferred high strength direction) and sandwich panels (consist of two strong and stiff sheets, or faces), separated by a layer of less dense material, or structure, or core, which has lower stiffness and lower strength.

In most cases composites consists of a bulk material (the matrix) and a reinforcement of some kind. So in another way, today's most man-made composites can be divided in to four main groups depending on the matrix material as [1]- (i) polymer matrix composites (PMC), (ii) metal matrix composites (MMC), (iii) ceramic matrix composites (CMC) and (iv) carbon and graphite matrix composites.

Thus composite materials are those, which are formed by the combination of one or more other materials with a polymer matrix to produce a material with a combination of desirable properties from individual components [1]. Thus, in addition, the constituent phases must be chemically dissimilar and separated by a distinct interface. In designing composite materials, scientists and engineers have ingeniously combined various metals, ceramics, and polymers to produce a new generation of extraordinary materials. Most composites have been created to improve combinations of mechanical characteristics such as stiffness, toughness, and ambient and high temperature strength. But in this study we have to choose only polymer matrix composites.

1.2. Organic-organic Conducting Composites

During the last decades, extensive international research efforts has followed the initial discovery of intrinsically conducting polymers (ICP's) containing repeating units of oxidized or reduced monomers, first reported by MacDiarmid and co-workers [3]. After that, the interest in ICP's has developed through three stages: (i) an initial interest motivated by their unique properties and practical possibilities; (ii) a decline in interest owing to difficulties in processing and poor mechanical properties; (iii) renewed interest following the discovery of solution and melt processibility of polyaniline (PANI) in the early 1990s [4-9]. In recent years, there has been some optimism that striking advances in understanding the chemistry and physics of ICP's [10] will support the development of large scale applications, witnessed by the award of the Nobel Prize in Chemistry to Heeger, MacDiarmid and Shirakawa in 2000. Manufacturers and researchers, who are actively involved in research and development in this field, have also recognized this trend. For example, some leading companies have discussed their strategy and advances in applications of ICP's at two European events: 'Commercializing Conductive Polymers' in February 2002 and 2003 in Brussels and Barcelona, respectively owing to their interesting electrical properties and their potential applications in various fields like electronics, microelectronics and medicine, corrosion protection [11], light emitting diodes (LEDs) [12], electro magnetic interference (EMI) shielding [13] and drug delivery [14], rechargeable batteries, gas separation membranes, antistatic agents and electroluminescent diodes (ELDs) [15-18], modified electrodes, chemical and

bio-sensors etc. Because of their important advantages most of the works with electrically conducting polymers have been focused on three main classes of polymeric materials viz. polyacetylene (PA) and its derivatives, polyphenylenes (PPh) and its derivatives, polyheterocyclics such as polypyrrole (PPy) and polythiophene (PTh) and polyaniline (PANI) etc. These polymers are relatively stable under ambient conditions and can be conveniently synthesized via oxidative or electro-chemical polymerization [19-22]. Oxidizing agents, such as iodine and $FeCl_3$, are convenient for oxidatively polymerizing monomers and to produce conductive polymers [21].

However, their poor mechanical properties and processibility constitute major obstacles to their extensive applications [23]. To improve the mechanical properties and processibility many kinds of method have been used, including the introduction of long alkyl groups into the main chain [24,25], the synthesis of soluble precursors [26,27], the preparation of conducting polymer composites [28] and so on [24,29]. Among these methods, the preparation of composites is the easier and more effective. In this consequent many kinds of conducting polymer composites, which combine the electrical conductivity of PPy, PANI, PTh and their derivatives with good mechanical properties of insulating polymers viz. polyethylene (PE) [29,30], PVC [31-34], poly(ethylene oxide) (PEO) [35,36], poly(vinyl alcohol) (PVAL) [37-41], poly(etherketone) (PEK) [42] poly(tetrahydrofuran) [43], polystyrene [44,45], polyurethane [46,47], ethylene vinyl acetate copolymer [48,49], polyamides and polyimide [50-53], rubber [54,55], polycarbonate [56] and poly(acrylonitrile) [57] have been reported.

This trend has been driven by the need to replace traditional inorganic conducting fillers and to improve the processibility of conducting polymers, along with their mechanical properties and stability. These composite materials have introduced conducting polymers to practical applications in different fields, including electromagnetic shielding and microwave absorption [58-61], static electricity dissipation [62-64], heating elements (clothing, wall papers, etc.) [65,66], conducting glues [67], conducting membrane materials [68,69], paint coatings for anticorrosion protection [70] and sensor materials [71,72].

As a consequence, conducting composites are very close to applications on a large scale for the industrial applications mentioned above [58-72]. Nevertheless, the choice of the best method to produce composites with specified characteristics remains an unresolved problem. The problem arises because the processing method may significantly determine the properties of the manufactured composite materials. Thus, our present discussion will be confined to the preparation and electrical properties of the composites of polyheterocyclics because of their attractive properties like relative ease of synthesis, good environmental stability and electrical conductivity.

1.3. Organic-inorganic Composite Materials

It is well-accepted fact that the progress of mankind today is directly or indirectly dependent on advanced technological materials (high performance materials) that perform better and open new dimensions in research and development. Among the major developments in materials in recent years are composite materials.

In fact, composites are now one of the most important classes of engineering materials, as they offer several outstanding properties as compared to conventional materials. These materials have found increasingly wider utilities in the general areas of chemical sensors, chromatography, fabrication of selective materials and electrical and optical applications.

Composite materials formed by the combination of inorganic materials and organic polymers are attractive for the purpose of creating high-performance or high functional polymeric materials. Of particular interest is the molecular level combination of two different components that may lead to new composite materials that are expected to provide different possibilities, termed "organic-inorganic hybrid" materials. These hybrid materials usually show properties intermediate between those of plastics and glasses (ceramics). Accordingly, hybrids can be used to modify organic polymer materials or to modify inorganic glassy materials. In addition to these characteristics, the hybrid materials can be considered as new composite materials that exhibit very different properties from their original components (organic polymers and inorganic materials), especially in the case of molecular level hybrids. Therefore, organic-inorganic composite materials are of intensive interest in the field of contemporary materials chemistry as these materials can exhibit synergetic extraordinary properties such as electrical, magnetic and optical properties [73], which arise from the synergism between the properties of the organic and inorganic components. There are several routes for the preparation of these materials, but probably the most prominent one is the incorporation of inorganic

building blocks in organic polymers by sol-gel process. These materials have gained much interest due to their remarkable change in properties such as mechanical [74], thermal [75-78], electrical [79] and magnetic [80] compared to pure organic polymers. Additionally, the properties of the composite materials depend on the morphology of the phases viz. organic and/or inorganic network, which has to be controlled over several length scales. Therefore, the development of such materials is a 'land of multidisciplinary' [81], where chemists, physicists, material scientists and engineers have to work closely together to fully exploit this technical opportunity for creating materials and device with benefits of the best of the two worlds namely inorganic and organic. Commencing a chemical point of view, one can distinguish between several ways to incorporate inorganic systems in organic polymers depending on the interactions between the moieties: materials with strong (covalent, coordination, ionic): weak (Van-der Waals, hydrogen-bonds, hydrophilic–hydrophobic balance) or without chemical interactions between the two components (Fig.1.3) [81,82]. Based on the structural distinction, Sanchez and Ribot classified the organic-inorganic hybrid materials into two classes [83].

Class I (network modifiers) in which the organic polymer or organic molecules are simply embedded into the inorganic matrix. No covalent bonds exist between both phases only weak interaction such as Van-der Walls forces, electrostatic or H-bonds. As an example of this class I are the organic dyes or biomolecules incorporated in the porous inorganic gel via the H bond between organic and inorganic parts the transparency and no phase separation could be achieved.

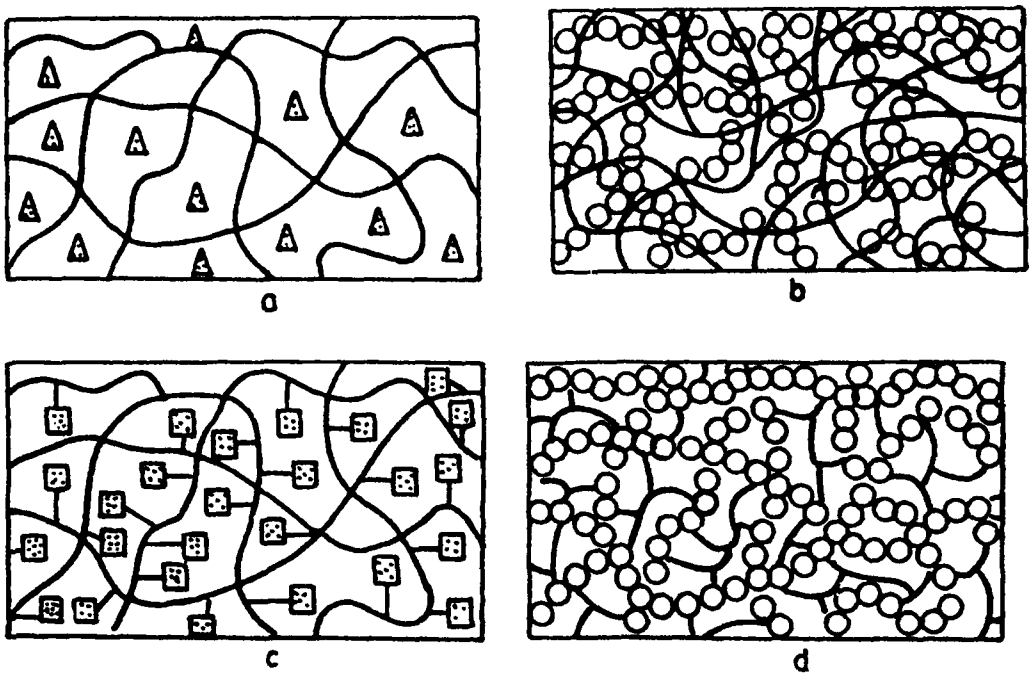


Fig. 1.3. Different kinds of inorganic–organic composite materials. (a) embedding of the inorganic moiety into the organic polymer, (b) interpenetrating networks (IPNs) with chemical bonds, (c) incorporation of inorganic groups by bonding to the polymer backbone and (d) dual inorganic-organic hybrid polymer.

Class II (network formers) in which the organic and inorganic parts establish covalent or iono-covalent bonds. To this class correspond the hybrid materials that incorporate fictionalized alkoxysilanes such as poly(dimethylsiloxane). This sol-gel method is extensively used to obtain amorphous materials where the homogeneity is directly designed on a molecular scale, ranging from single-phase to multi-phase systems. The combination of several precursors for the synthesis of nanostructured materials hybrid polymers are an open door in the chemical route and can be used to form nanoparticles, coating, fibers or bulk solids with the corresponding technological applications.

Hybrid materials made in this way are termed creamers (ceramic polymers), ormosils (organically modified silicates) or ormocers (organically modified ceramics) [84]. Through the combinations of different inorganic and organic components in conjunction with appropriate processing methods, various types of primary and secondary bonding can be developed leading to materials with unique combination of properties which cannot be achieved by other materials. The concept of 'molecular level mixing' between two different materials can also be considered. Since the late 1980s, molecular level combination between organic polymers and inorganic materials has been of interest. Review articles concerning hybrid materials have been reported by *Saegusa* and *Chujo* [85], *Sanchez* and *co-workers* [81,83], *Schubert et al.* [86], *Novak* [87], *Loy and Shea* [88], *Mark* [89], *Johan N Hay* and *Steve J Shaw* [90] and others [91]. During this period, the study of organic-inorganic hybrid materials focused on the following points: firstly, exploration of new preparative

methodology for hybrid materials; secondly, new combinations between different materials; thirdly, functionalization of hybrid materials; and fourthly, modifications of hybrids for industrial applications. It is necessary to point out some important composite materials that are believed to have evolved and will result in interesting molecular hybrid materials in the near future. But due to numerous papers published on polymer organic–inorganic composite materials, it is impossible to completely review this field. Therefore, this review will focus on the most common principal concepts used to incorporate organic systems into an inorganic polymeric matrix and the resulting properties of such materials. The reader is referred to the literature cited for a more detailed description.

1.3.1. Organic-inorganic composite synthesis strategies

Although chemists from the sol-gel scientific community initially have worked out organic-organic and/or organic-inorganic composites and have attracted a great deal of attention in material science, but at the time of advancement in materials composites are elaborated by researchers coming from a variety of disciplines, polymers chemists, solid-state chemists, catalysis and material researchers etc. Each of these communities elaborate composites using their own tools, specific disciplinary methods and more important their own raw materials. It is not seldom to see that a polymer chemist will work out a composite system having an emphasis on the polymer side of the composite, using even pre-formed polymers, capped oligomers etc. Sol-gel and inorganic chemists will preferably use as precursors, silicon or metal alkoxides or even inorganic building units such as clusters or

nanoparticles. They can also use lamellar inorganic compounds as host for organic components. Many names have been given to these materials: ceramers, polycerams, ormosils or ormocers. These names were labeled by materials science researchers coming from different sides (polymers scientists, glass or ceramic scientists, organometallic scientists). However it is now commonly accepted that a molecular approach for the synthesis of hybrids reflects better the wide opportunities offered by this compounded chemistry. Thus, a critical challenge in the design of these hybrid organic-inorganic and/or inorganic-organic systems is a control of mixing between the two dissimilar phases.

1.4. Chromatography

It was the Russian botanist *Mikhail Tsvet* (Mikhail Semyonovich Tsvet), who invented the first chromatography technique in 1901 during his research on chlorophyll. He used a liquid-adsorption column containing calcium carbonate to separate plant pigments. The method was described on December 30, 1901 at the XI Congress of Naturalists and Doctors in St. Petersburg. The first printed description was in 1903, in the Proceedings of the Warsaw Society of Naturalists, section of biology. He first used the term chromatography in print in 1906 in his two papers about chlorophyll in the German botanical journal, *Berichte der Deutschen Botanischen Gesellschaft*. In 1907 he demonstrated his chromatograph for the German Botanical Society. The phenomenon of precipitational separation was observed before Tsvet as well. His contribution was turning the phenomenon into the method of scientific analysis. The Greek word *chroma* in *chroma*tography means

color in English and refers both to Tsvet's name that is literally translated from Russian as *color* and to the color of the plant pigments he was separating at that time. In 1952 *Archer John Porter Martin* and *Richard Laurence Millington Synge* were awarded the Chemistry *Nobel Prize* "for their invention of partition chromatography" [92]. The technology of chromatography advanced rapidly throughout the 20th century and ***Chromatography*** became a family of analytical chemistry techniques for the separation of mixtures. It involves passing the sample, a mixture which contains the analyte, in the "mobile phase", often in a stream of solvent, through the "stationary phase". The stationary phase retards the passage of the components of the sample. When components pass through the system at different rates they become separated in time, like runners in a mass-start foot race. Each component has a characteristic time of passage through the system, called a "retention time". Chromatographic separation is achieved when the retention time of the analyte differs from that of other components in the sample. In accordance, researchers found that the principles underlying Tsvet's chromatography could be applied in many different ways, giving rise to the different varieties of chromatography described below. Simultaneously, advances continually improved the technical performance of chromatography, allowing increasingly similar molecules to be resolved.

1.4.1. Types of chromatography

As for as the knowledge of Human civilization concerned to the science and technology, a wide variety of instrumental and non-instrumental chromatographic techniques have been developed since the pre historic time. As the field is very

diverse it is very difficult to summarize all the chromatographic techniques. Therefore, we have chosen to only some non-instrumental techniques in short and particularly ion-exchange chromatography in details. A brief principles and methods of non-instrumental chromatographic techniques are given below.

1.4.1.1. Liquid chromatography

Simple liquid chromatography consists of a column with a fitted bottom that holds a stationary phase in equilibrium with a solvent. Typical stationary phases (and their interactions with the solutes) are: *solids* (adsorption), *liquids on an inert solid support* (partitioning), *porous inert particles* (size-exclusion) and *ionic groups on a resin* (ion-exchange). The mixture to be separated is loaded onto the top of the column followed by more solvent. The different components in the sample mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase. The compounds are separated by collecting aliquots of the column effluent as a function of time. Schematic diagram of a simple liquid chromatographic separation is given in Fig. 1.4.

1.4.1.2. Adsorption chromatography

Adsorption chromatography is probably one of the oldest types of chromatography around. It utilizes a mobile liquid or gaseous phase that is adsorbed onto the surface of a stationary solid phase. The equilibration between the mobile and stationary phase accounts for the separation of different solutes. Typical chromatogram is given in Fig. 1.5.

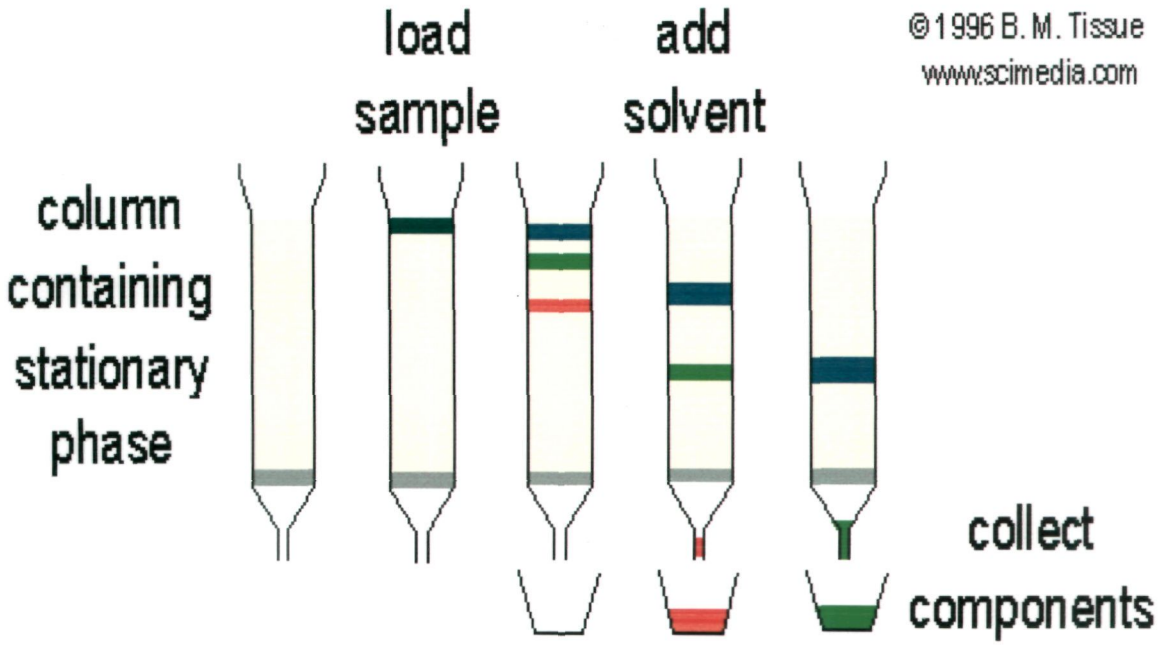


Fig. 1.4. Schematic diagram of a simple liquid chromatographic separation.

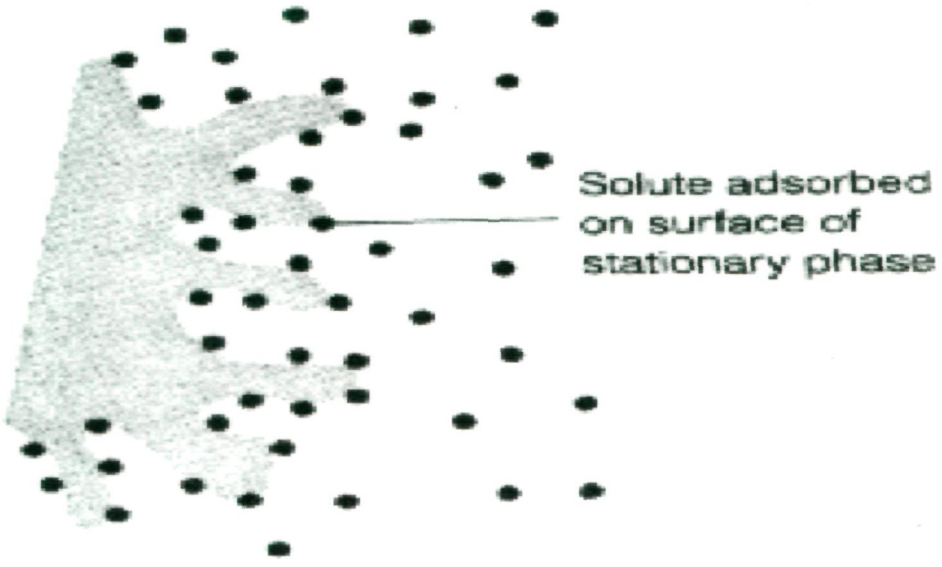


Fig. 1.5. Typical chromatogram of adsorption chromatography.

1.4.1.3. Paper chromatography

In paper chromatography, chemical interactions with the paper make compounds travel at different rates. Therefore, A small spot of solution containing the sample is applied to a strip of chromatography paper about one centimeter from the base. This sample is *adsorbed* onto the paper. This means that the sample will contact the paper and may form interactions with it. Any substance that will react with (and thus bond to) the paper cannot be measured using this technique. The paper is then dipped in to a suitable solvent (such as ethanol or water) and placed in a sealed container. As the solvent rises through the paper it meets the sample mixture, which starts to travel up the paper with the solvent. Different compounds in the sample mixture travel different distances according to how strongly they interact with the paper. A chemical interaction with the paper to demonstrate compounds travel is shown in Fig. 1.6. Paper chromatography takes some time and the experiment is usually left to complete for some hours.

1.4.1.4. Thin layer chromatography (TLC)

Thin layer chromatography (TLC) is a standard laboratory method in organic chemistry. Because of its simplicity and speed TLC is often used for monitoring chemical reactions and for the qualitative analysis of reaction products. This process is similar to paper chromatography with the advantage of faster runs, better separations, and the choice between different adsorbents. In this chromatography the stationary phase consists of a thin layer of adsorbent like silica gel, alumina or cellulose on a flat carrier like a glass plate, a thick aluminum foil, or a plastic sheet.

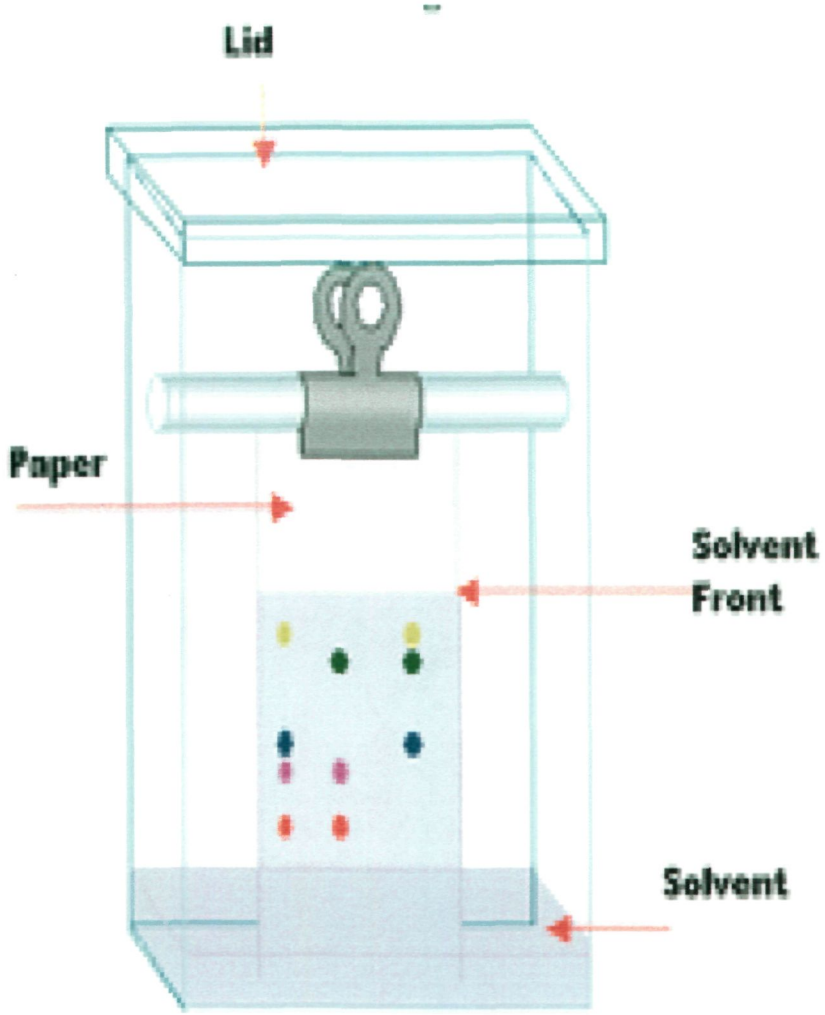


Fig. 1.6. A chemical interaction with the paper to demonstrate compounds travel.

TLC plates are made by mixing the adsorbent with a small amount of inert binder like calcium sulphate (gypsum) and water, spreading the thick slurry on the carrier, drying the plate, and activation of the adsorbent by heating in an oven. The thickness of the adsorbent layer is typically around 0.1–0.25 mm for analytical purposes and around 1–2 mm for preparative TLC.

Several methods exist to make colorless spots visible:

- Often a small amount of a fluorescent dye is added to the adsorbent that allows the visualization of UV absorbing spots under a black light 'UV_{254}'.
- Iodine vapors are a general unspecific color reagent.
- Specific color reagents exist into which the TLC plate is dipped or which are sprayed onto the plate.

Once visible, the spots can be quantified by way of calculating their R_f values. These values should be the same regardless of the extent of travel of the solvent, and in theory are independent of a single experimental run. They do depend on the solvent used, and the type of TLC plate. A chromatogram showing separation of black ink on a TLC plate is given in Fig. 1.7.

1.4.1.5. Partition chromatography

This form of chromatography is based on a thin film formed on the surface of a solid support by a liquid stationary phase. Solute equilibrates between the mobile phase and the stationary liquid as given in Fig. 1.8.

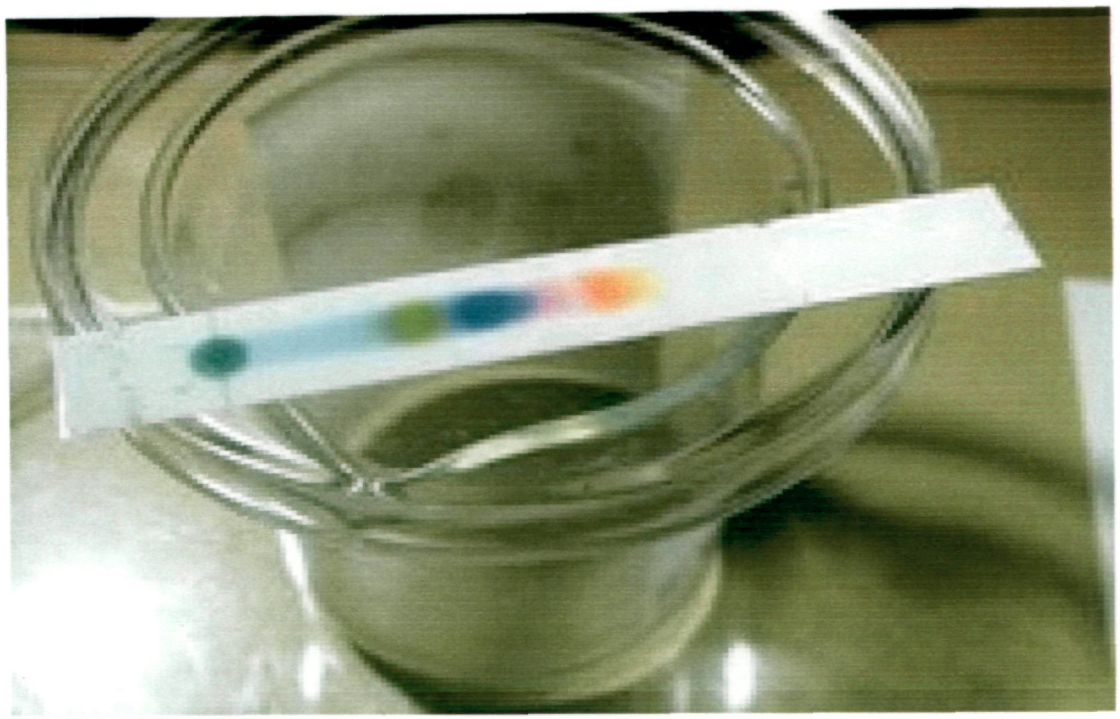


Fig. 1.7. A chromatogram showing separation of black ink on a TLC plate.

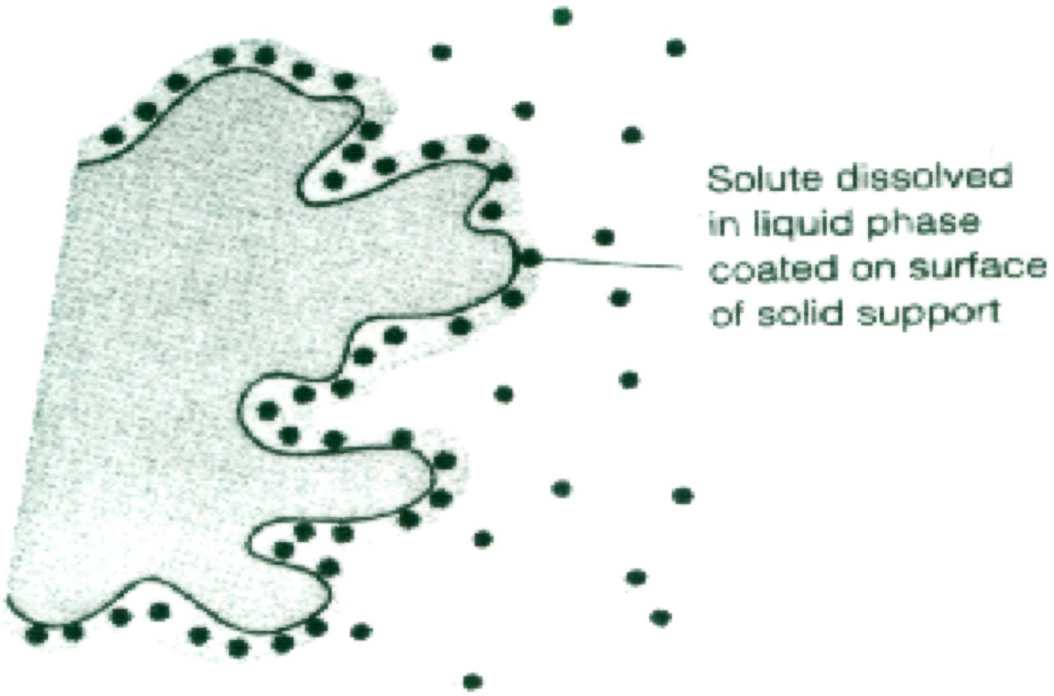


Fig.1.8. Typical chromatograms of partition chromatography indicating solute equilibration between the mobile phase and the stationary liquid.

1.4.1.6. Molecular exclusion chromatography

Molecular exclusion or size exclusion chromatography, also called gel-permeation chromatography (GPC), uses porous particles to separate molecules of different sizes. It is generally used to separate biological molecules and to determine molecular weights and molecular weight distributions of polymers. Molecules that are smaller than the pore size can enter the particles and therefore have a longer path and longer transits time than larger molecules that cannot enter the particles. All molecules larger than the pore size are unretained and elute together. Molecules that can enter the pores will have an average retention time in the particles that depends on the molecules size and shape. Different molecules therefore have different total transit times through the column. Typical chromatographs are shown in Fig. 1.9.

1.4.1.7. Affinity chromatography

This is the most selective type of chromatography employed. It utilizes the specific interaction between one kind of solute molecule and a second molecule that is immobilized on a stationary phase. For example, the immobilized molecule may be an antibody to some specific protein. When solute containing a mixture of proteins are passed by this molecule, only the specific protein is reacted to this antibody, binding it to the stationary phase as shown in Fig. 1.10. This protein is later extracted by changing the ionic strength or pH.

1.4.1.8. Column chromatography

Column chromatography utilizes a vertical glass column filled with some form

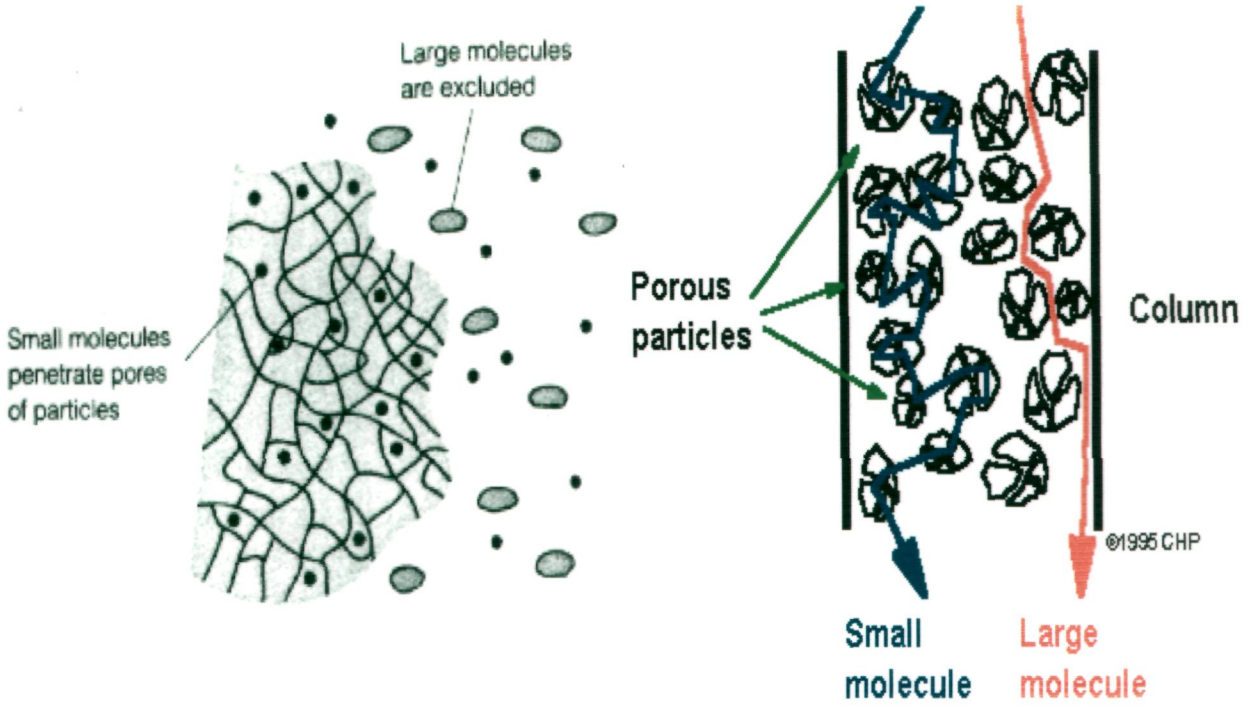


Fig. 1.9. Two different schematic of molecular exclusion chromatographic columns.

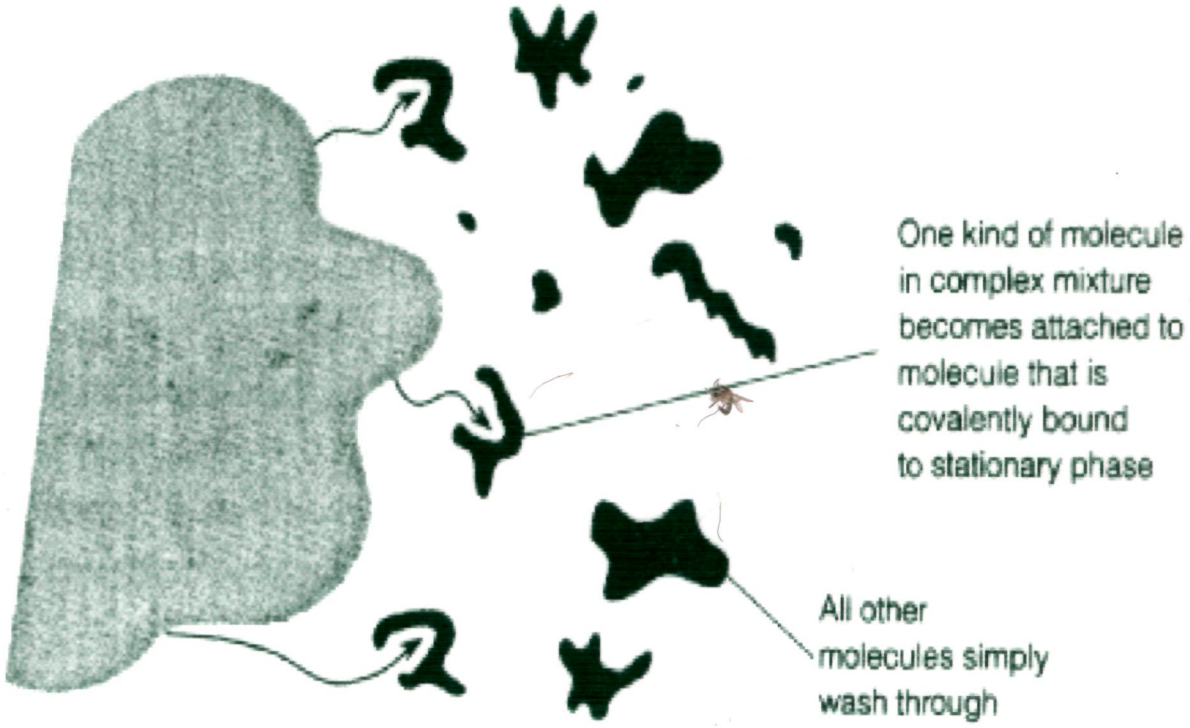


Fig. 1.10. Typical chromatogram of affinity chromatography.

of solid support with the sample to be separated placed on top of this support. The rest of the column is filled with a solvent which, under the influence of gravity, moves the sample through the column. Similarly to other forms of chromatography, differences in rates of movement through the solid medium are translated to different exit times from the bottom of the column for the various elements of the original sample.

In 1978, W.C. Stills introduced a modified version of column chromatography called **flash column chromatography** "flash". The technique is very similar to the traditional column chromatography, except for that the solvent is driven through the column by applying positive pressure. When applying positive pressure on top of the column, most separations could be performed in less than 20 minutes with improved separations compared to the old method. This makes flash column chromatography the method of choice for most synthetic organic chemists when purifying organic compounds. In the modern flash chromatography systems which can be purchased, the glass columns are replaced with pre-packed plastic cartridges. Solvent is pumped through the cartridge, which is much quicker. Systems may also be linked with detectors and fraction collectors providing automation. The introduction of gradient pumps means quicker separations and less solvent usage. A picture of a standard column chromatography and a flash column chromatography setup is shown in Fig. 1.11.

1.4.1.9. Ion-exchange chromatography

Ion-exchange chromatography is a column chromatography that uses an oppositely charged stationary phase to the sample ion and is used almost exclusively

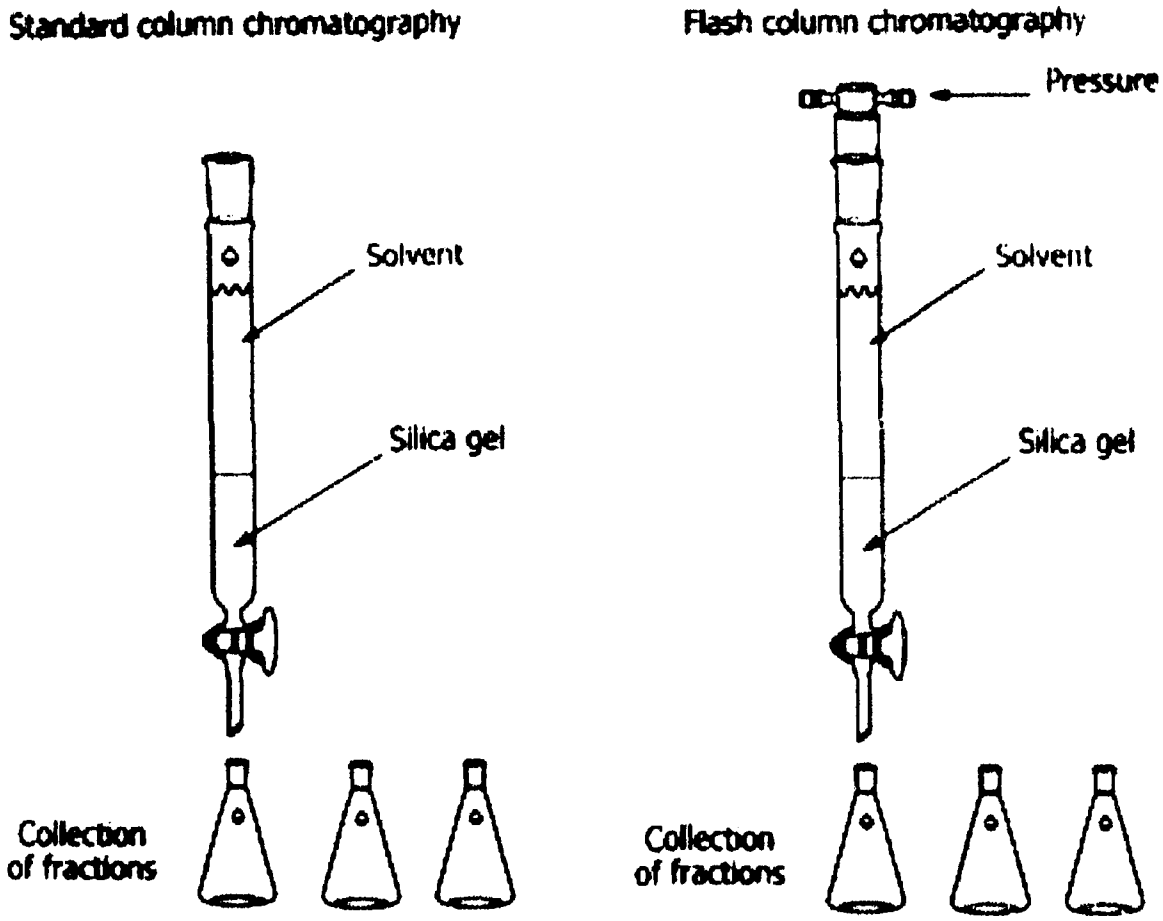


Fig. 1.11. A picture of a standard column chromatography and a flash column chromatography setup.

with ionic or ionizable samples. The stronger the charge on the sample, the stronger it will be attracted to the ionic surface and thus, the longer it will take to elute because solute ions of the opposite charge in the mobile liquid phase are attracted to the resin by electrostatic forces and the mobile ions held near cations that are covalently attached to the stationary phase as shown in Fig. 1.12. In particular, the stationary phase is usually anion-or cation-exchange resin that carries charged functional groups, which interact with oppositely charged groups of the compound to be retained:

- Positively charged ion-exchanger (*anion-exchanger*) interacts with anions.
- Negatively charged ion-exchanger (*cation-exchanger*) interacts with cations.

However, ion-exchange chromatography is a type of liquid chromatography in which ion-exchange process takes place. It has found numerous applications in science and industry, and is, at present, the most important analytical tool in environmental analysis, such as, in the recovery of the precious metals from industrial effluents, removal of arsenic and heavy toxic metal ions, recovery of important organics from paper, wine, cigarette and food processing industries, recovery of radioactive isotopes, separation and analysis of inorganics in the environment. Many classical methods have been greatly speeded up by the use of an ion-exchange process. In view of above-mentioned fact we have also planed to study in the field of ion-exchange chromatography.

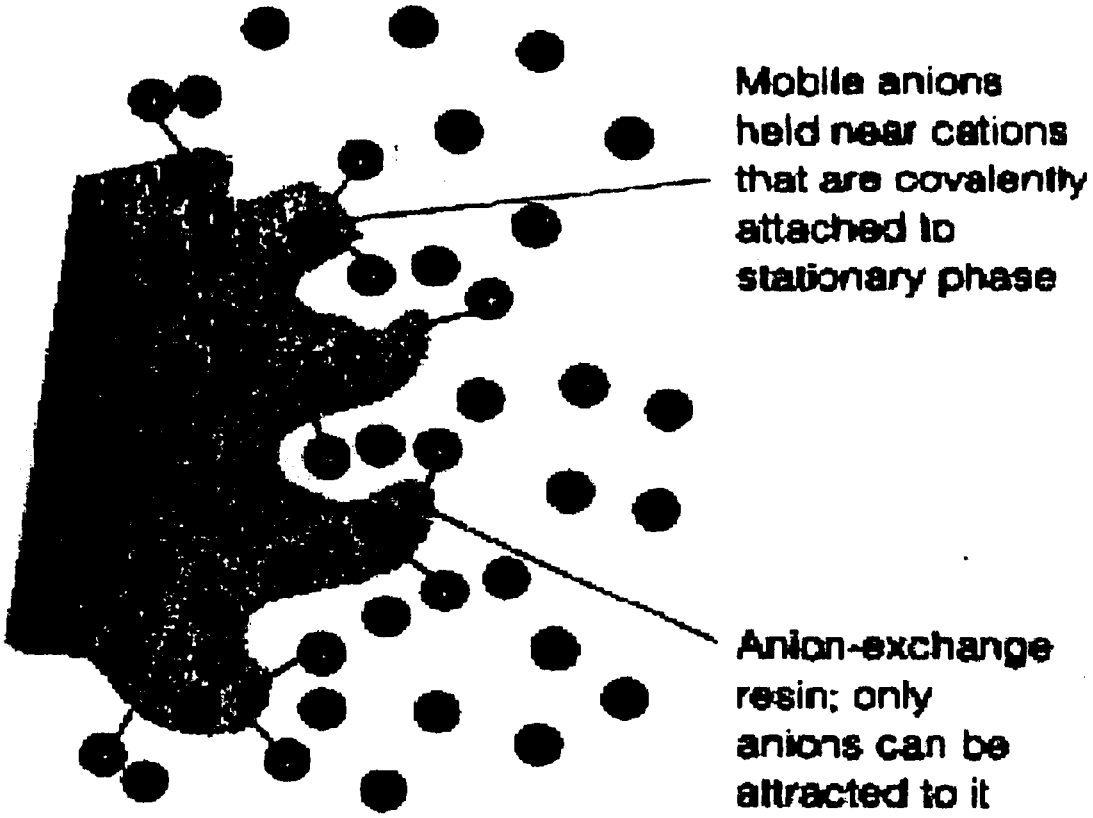


Fig. 1.12. Ion-exchange chromatography.

1.5. Ion-Exchange Properties of Materials

1.5.1. Ion-exchange phenomenon & its historical background

The phenomenon of ion-exchange is not of a recent origin. Many million years ago it had occurred in various sections of the globe. For example, some ions like potassium and lithium of patalite of pegmatite veins had been replaced with rubidium and cesium ions of step wisely fluid from the maga. This is nothing but ion-exchange phenomenon between minerals like patalite (solid phase) and fused salt fluid (liquid phase) [93]. It is well known that ion-exchange has been playing very important roles during the course of weathering; aqueous rocks, clay rocks and soils being very effective ion-exchangers. Since life had been created in the sea, ion-exchange through bio-membranes between living organs and outside matters has been giving the essential motive forces to life and its evolution. The earliest of the references were found in the Holy Bible establishing Moses's priority that succeeded in preparing drinking water from brackish water [94], by an ion-exchange method. Later on, Aristotle found the seawater loses part of its salt contents when percolated through certain sand [95]. In Egypt and Greece as well as in China, ancient people were clever enough to use some soils, sands, natural zeolites and plants as the tools for improving the quality of drinking water by way of desalting or softening. However, they were not aware of the actual phenomenon occurring in the process. Basically, ion-exchange is a process of nature occurring throughout the ages before the dawn of civilization, has been embraced by analytical chemists to make use of difficult separation easier and possible.

Francis Bacon in 1623 brought the intentional use of ion-exchange, without knowledge of its theoretical nature, based purely on empirical experiences and he described a method for removing salts from seawater. The first half of the 19th century was characterized by the appearance of the first information leading to the discovery of the ion-exchange principle, based primarily on the work of soil chemists. *Thompson* and *Way* in 1850 described independently that calcium and magnesium ions of certain types of soils could be exchanged for potassium and ammonium ions [96,97]. They defined the special properties of soil as *'base exchange'*. In the second half of the 19th century, agro chemists published a great number of papers dealing with ion-exchange in soils. *Eichorn* (in 1858) demonstrated exchange processes are reversible in soils [98]. In 1859, *Boedecker* proposed an empirical equation describing the establishment of equilibrium on inorganic ion-exchange sorbents. In the 20th century, the majority chemists believed that the *'base exchange'* in soils is nothing but a sort of absorption. Strong supports to ion-exchange come out with the synthesis of materials from clay, sand and sodium carbonate by *Gans* [99].

The discovery and development of the theory of ion exchange was reflected in practical applications. *Gans* [99] developed the basis for the synthesis and technical application of inorganic cation-exchangers at the beginning of the 20th century. He termed the amorphous cation-exchangers based on aluminosilicate gels "permutites", having broad application, were actually the first commercially available ion-exchangers. In 1917, *Folin* and *Bell* developed an analytical method based on these

materials for the separation and collection of ammonia in urine [100]. However, the usefulness of these synthetic zeolites was limited because of their low chemical and mechanical stability, ion-exchange capacity that led the chemists to seek alternatives. During the period between the 1930s and 1940s, inorganic ion-exchange sorbents were replaced in almost all fields by the new organic ion-exchangers. The observation of *Adam* and *Holms* [101] that the crushed phonograph records exhibit ion-exchange properties, eventually resulted in the more significant development of synthetic ion-exchange resins (high molecular weight organic polymers containing a large number of ionic functional groups) in 1935. No scientist could then neglect ion-exchange phenomenon. However, it took nearly 85 years for the ion-exchange phenomenon to be fully recognized in chemistry since its scientific finding and understanding by *Thompson* and *Way*.

Just as applications of the organic resins are limited by breakdown in aqueous systems at high temperatures and in presence of high ionizing radiation doses; for these reasons there had been a resurgence of interest in inorganic exchangers in the 1950s. One of the possible ways of solving these problems involved replacing the organic skeleton of the ion-exchanger by an inorganic skeleton. Pioneering work was carried out in this field by the research team at the Oak Ridge National University led by *Kraus*, and by the English team led by *Amphlett*.

Further extensive research and study of inorganic ion-exchange sorbents were carried out in the 1960s and 1980s from the original amorphous type of ion-exchange sorbents to the study of crystalline ion-exchange materials. Clearfield and co-workers

made great contributions in this area. Since last two decades, intense research has continued on the synthesis of a number of new 'organic-inorganic' composite materials having excellent properties that not only met the requirements of modern laboratories but also led to solution of previously insolvable problems. An interest of inorganic as well as composite ion-exchange materials in ion-exchange operations in industries is increasing day by day as their field of applications is expanding.

1.5.2. Ion-exchange process and its mechanism

The ion-exchange process became established as an analytical tool in laboratories and in industries, as it was studied chiefly by practical chemists interested in effects and performance *etc*. The primary condition of an ion-exchange process is the stoichiometry. In organic resins, it is an established fact [102]. The exchange of ion takes place stoichiometrically, really by the effective exchange of ions between two immiscible phases, stationary and mobile. A typical ion-exchange reaction may be represented as follows:

$$\overline{AX} + B\,(aq) \rightleftharpoons \overline{BX} + A\,(aq) \qquad \ldots\ldots 1.1$$

where A and B (taking part in ion-exchange) are the replaceable ions, and X is the structural unit (matrix) of the ion-exchanger. Bar indicates the exchanger phase and (aq) represents the aqueous phase.

In order to describe equilibria and to understand the mechanism of an ion-exchange process occurring on the surface of exchanger and to evaluate its theoretical behavior, it is important to have a study of its kinetics and thermodynamics. Since inorganic ion-exchangers possess a rigid matrix they do not

swell appreciably and hence such studies are simpler to perform on them as compared to the organic resins that swell appreciably. Ion-exchange equilibrium may be described by two theoretical approaches *viz.* (i) *Based on law of mass action, and* (ii) *Based on Donnan theory.*

From the theoretical point of view the *Donnan theory* has an advantage of permitting a more elegant interpretation of thermodynamic behavior in an ion-exchanger. Probably, the first time, quantitative formation of ion-exchange equilibria was made by *Gane* [103] using the mass action law in its simplest form without involving the concept of activity coefficients. This concept was further accounted by *Kielland* [104] and finally, a suitable choice of general treatment was given by *Gaines* and *Thomas* [105]. Many workers have studied the thermodynamics of cation-exchange on zirconium(IV) phosphate [106-109]. In a series of papers, the effect of crystallinity on the thermodynamics of ion-exchange of alkali metal ions/H^+ ions on the samples of α-zirconium phosphate was examined. Ion-exchange isotherms and calorimetric heats of exchange were determined on samples varying from amorphous to highly crystalline [110-114].

However, from the practical point of view, the mass action approach is simpler. *Nancollas* and *coworkers* [115,116] have interpreted the thermodynamical functions in term of the binding nature between alkali metals and the ion exchange matrix. The ion-exchange equilibria of Li(I), Na(I) and K(I) on zirconium(IV) phosphate have also been studied by *Larsen* and *Vissers* [117], who calculated the equilibrium constants and other thermodynamical parameters *viz.* ΔG^o, ΔH^o and ΔS^o.

Similar studies have been made on anion-exchangers also [118]. Ion-exchange equilibria of alkaline earth metal ions on different inorganic ion-exchangers such as tantalum arsenate [119], iron(III) antimonate [120], antimony(V) silicate [121,122], zirconium(IV) phosphosilicate [123,124] and alkali metal ions on iron(III) antimonate [125] and α-cerium phosphate [126] were studied. Other interesting thermodynamic studies relate to the adsorption of pesticides on inorganic and composite ion-exchangers have also been studied in these laboratories [127,128]. The study has revealed that the adsorption is higher at lower temperature and the presence of an ion-exchange material in soil greatly enhances its adsorption capability for the pesticides. *Nachod* and *Wood* [129] have made the first and detailed attempt on kinetic studies of ion-exchange. They have studied the reaction rate with which ions from solutions are removed by a solid ion-exchanger or conversely the rate with which the exchangeable ions are released from the exchanger. Later on *Boyd et al.* [130] have studied the kinetics of metal ions upon the resin beads and have given a clear understanding about the particle and film diffusion phenomenon that govern the ion-exchange processes. The former is valid at higher concentrations while the later at lower concentrations. The kinetic of metal ions on sulphonated polystyrene has been studied by *Reichenberg* who again confirmed that at high concentrations the rate is independent of the ingoing ion (particle diffusion); while at low concentrations the reverse is true (film diffusion).

1.5.3. Ion-exchange materials: An introduction and literature review

1.5.3.1. Inorganic ion-exchange materials

1.5.3.1.1. Natural inorganic ion-exchangers

Many natural mineral compounds, such as clays (*e.g.* bentonite, kaolinite and illite), vermiculite and zeolites (*e.g.* analcite, chabazite, sodalite and clinoptilolite), exhibit ion-exchange properties. Natural zeolites were the first materials to be used in ion-exchange processes. Clay minerals are often employed as backfill or buffer materials for the radioactive waste disposal sites because of their ion-exchange properties, low permeability and easy workability. Clay can also be used in batch ion-exchange processes but are not generally suited to column operation because their physical properties restricts the flow through the bed. In 1985 British Nuclear Fuels Plant (BNFP), successfully commissioned the Site Ion Exchange Effluent Plant (SIXEP), which use naturally occurring clinoptilolite to remove cesium and strontium from fuel cooling pond water [131]. Other natural aluminosilicate materials, such as green sand, are also used in some waste treatment applications, generally in column or large deep bed designs. In this capacity they can be used as a combination of an ion-exchanger and particulate filler. Clay minerals and natural zeolites, although replaced by synthetics to a large extent, continue to be used in some applications, owing to their low cost and wide availability.

The main disadvantages of natural inorganic ion-exchangers are:

- Their relatively low exchange capacities;
- Their relatively low abrasion resistance and mechanical durability;

- Their non-controllable pore size;
- That clay minerals tend to peptize (i.e. convert to a colloidal form);
- That zeolites are difficult to size mechanically;
- That they can be partially decomposed in acids or alkalis;
- That, owing to their limited chemical stability in many solutions, especially those with a very low salt content, they sometimes need a chemical or thermal pretreatment;

1.5.3.1.2. Synthetic inorganic ion-exchangers

Synthetic ion-exchangers are produced by creating chemical compounds with the desired physical and chemical properties. On the basis of chemical characteristics synthetic inorganic ion-exchangers are classified as follows:

- Synthetic zeolites (aluminosilicates)
- Hydrous oxides of metals
- Acidic salts of polyvalent metals
- Insoluble salts of heteropolyacids
- Insoluble hydrated metal hexacyanoferrate (II) and (III) (ferrocyanides)
- Other substances with weak exchange properties

Zeolites were the first inorganic materials to be used for the large-scale removal of waste effluents. Zeolites are crystalline alumino-silicate based materials and can be prepared as microcrystalline powders, pellets or beads. The main advantages of synthetic zeolites when compared with naturally occurring zeolites are

that they can be engineered with a wide variety of chemical properties and pore sizes, and that they are stable at higher temperatures.

The main limitations of synthetic zeolites are that:

- They have a relatively high cost compared with natural zeolites;
- They have a limited chemical stability at extreme pH ranges (either high or low);
- Their ion specificity is susceptible to interference from similar sized ions;
- The materials tend to be brittle, which limits their mechanical stability;

The selectivity and capacity of zeolites can provide a satisfactory processing of low strength salt solutions. The actual processing capacities obtained with zeolites are lower than their maximum capacities since the bed is changed at the early stages of breakthrough and because the waste streams usually contain other ions that will occupy some of the exchange sites and therefore reduce the processing capacity. Synthetic silica based ion-exchangers were produced for technical purpose by fusing soda, potassium carbonate, feldspar and kaolinite (Schmaltz permutite) and later from aluminum sulfate solution containing sodium silicate by precipitation with sodium hydroxide solution (Gel permutite). Since then artificial crystalline zeolites have also been successfully synthesized. The advantageous properties of the crystalline silicate based ion-exchanger with the modern synthetic resin based ion-exchangers are as follows: they are less sensitive to higher temperatures, their structure are stiff and uniform and they are therefore more selective and suitable for separation of ions on the basis of their different sizes. Because of this, some of them are now also used as

ionic or molecular sieves. In India a systematic investigation has been carried out to evaluate the performance of locally available synthetic zeolites for the removal of cesium, strontium and thorium from solution [132-134]. The zeolites, after exchange with cesium, strontium or thorium, were thermally treated to fix the ions successfully in the same matrix [135]. A locally available synthetic mordenite was used recently in a campaign to reduce activity in spent fuel storage pool water [136].

Hydrous oxides are of particular interest because most of them can function both cation and anion-exchangers, and at certain conditions, as amphoteric exchangers. Their dissociation may be schematically represented as follows:

$$M-OH \longrightarrow M^{+} + OH^{-} \quad \text{..... 1.2}$$

$$M-OH \longrightarrow M-O^{-} + H^{+} \quad \text{..... 1.3}$$

(M represents the central atom)

Scheme '1.2' is favored by acid conditions when the substance can function as anion-exchanger, and scheme '1.3' by alkaline conditions, when the substance can function as cation-exchanger. Near the isoelectric point [137], dissociation according to both schemes can take place and both type of exchange may occur simultaneously. The hydrous oxides may be divided into two main types termed particle hydrates and framework hydrates [138]. Particle hydrates are both cation and anion-exchangers. Most of the group 3,4,13, and 14 metals form hydrous oxides that belong to this group. Metals in groups 5 and 15 in their higher oxidation states generally form framework hydrates. The pyrochlore nature (Fig. 1.13) of crystalline hydrous antimony(V) oxide exchanger was revealed by powder X-ray diffraction, which was

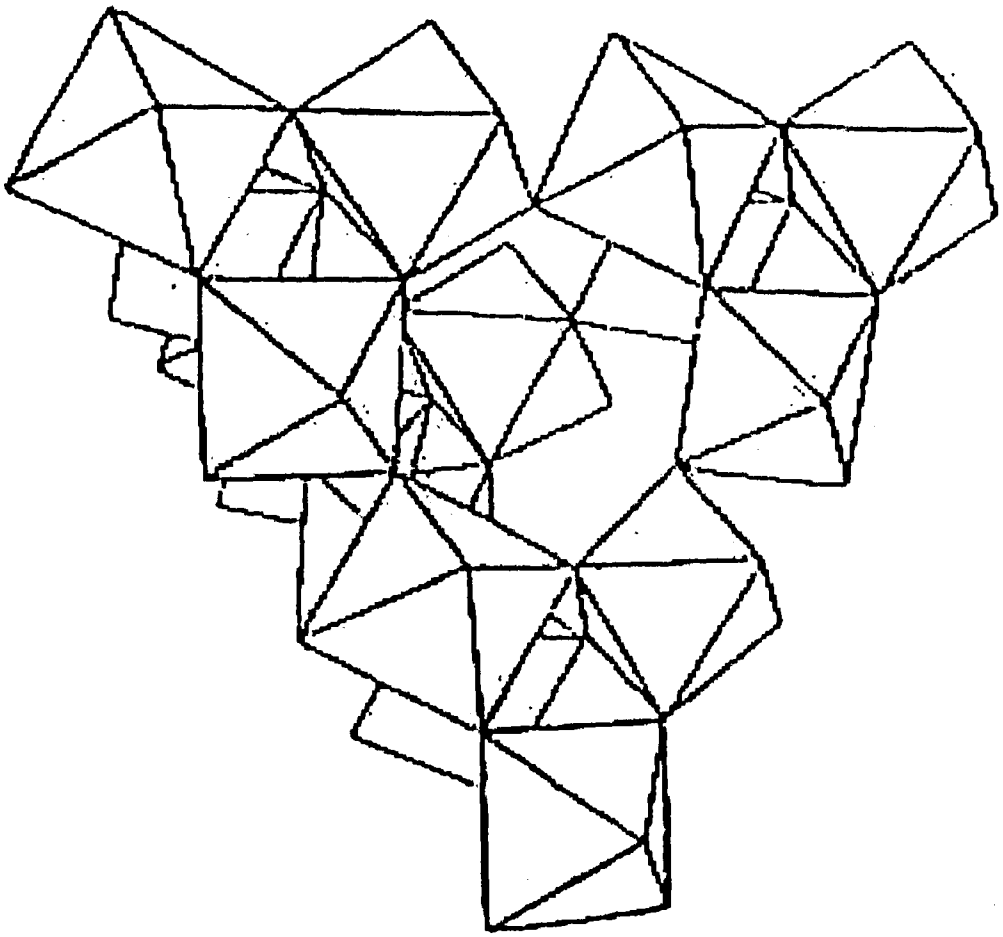


Fig. 1.13. Schematic diagram of the pyrochlore framework formed by antimonic acid, $(H_3O^+)_2\,Sb_2O_6$ showing the formation of a hexagonal shaped tunnel. Exchangeable H_3O^+ ions reside within the tunnels.

established the composition as $(H_3O)_2Sb_2O_6$ .xH_2O [138]. While the mixed metal oxide of the pyrochlore structure are also being obtained [139] as shown in Fig. 1.14. As a consequence cation-exchange selectivities are affected and metal ion uptake can be increased [140-142]. Layered double hydroxides (LDHs) (Fig. 1.15) constitute an interesting and extensive class of layered compounds [143]. An excellent review on LDHs has been published by *deRoy et al.* [144].

Acidic salts of multivalent metals form by mixing the solutions of the salts of III and IV group elements of the periodic table with the more acidic salts. These salts, acting generally as cation-exchangers, are gel like or microcrystalline materials and possess mostly a high chemical, thermal and radiation stability.

Salts of heteropolyacids have a general formula $H_mX.Y_{12}O_{40}.$ nH_2O, where m = 3, 4 or 5, X can be phosphorous, arsenic, silicon, germanium or boron and Y, one of the elements such as molybdenum, tungsten or vanadium. The salts of heteropolyacids with small cations are more soluble in comparison to the salts with large cations. Their hydrolytic degradation occurs in strongly alkaline solutions.

Insoluble ferrocyanides can be precipitated by mixing the metal salt solutions with $H_4[Fe(CN)_6]$, $Na_4[Fe(CN)_6]$, or $K_4[Fe(CN)_6]$ solutions. The composition of such precipitates may depend on the acidity, order of mixing and the initial ratio of the reacting components. They are chemically stable in acid solutions up to a concentration of 2 M. Cu and Co ferrocyanides have been found to be radiation resistant. They have found various applications in analytical chemistry and in technological practice because of their highly selective ion-exchange behavior and

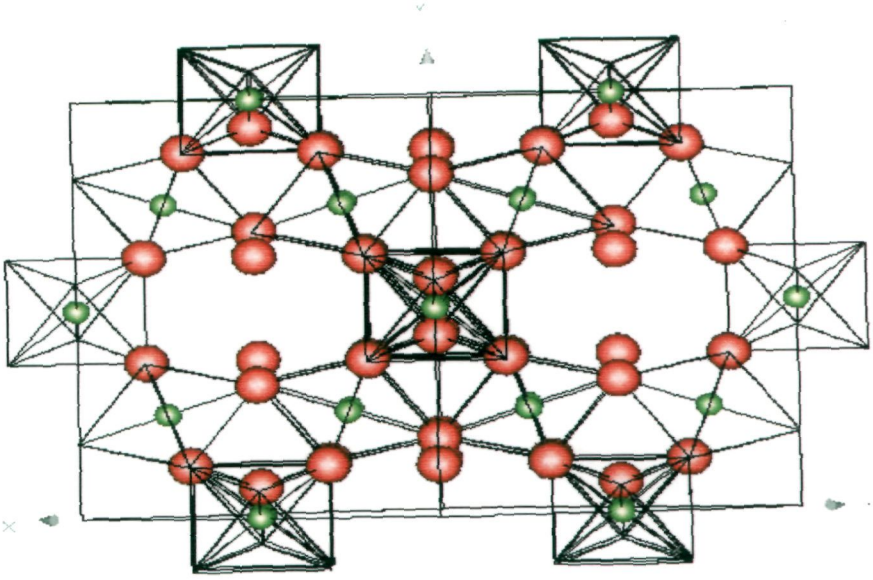


Fig. 1.14. Structure of Ti-antimonate (pyrochlore) viewed along the edge of the cubic unit cell. Structure refinement carried out using powder XRD and Rietveld method with GSAS program suite. Large red spheres: O. Small green spheres: Ti or Sb .

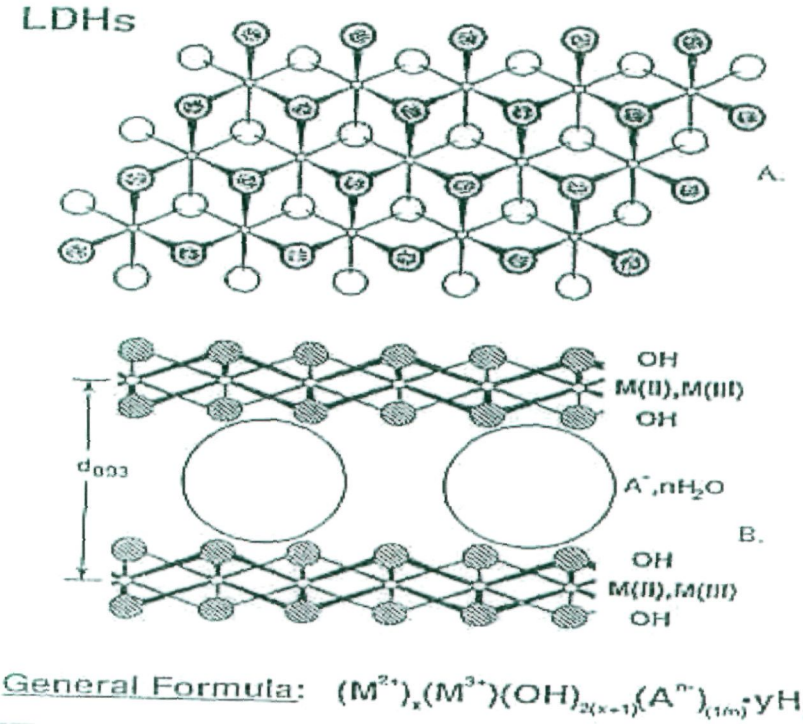


Fig. 1.15. Schematic representation of a layered double hydroxide (LDH). (A) Top view of brucite layer. (B) Side view showing anions between the brucite like layers.

chemical and mechanical stability. In India potassium cobalt(II)–hexacyanoferrate(II) has emerged as a promising inorganic sorbent that can be prepared in a column-usable granular form that needs no resin support. A 5 L column of sorbent was recently used to reduce the ^{137}Cs activity in 12,000 L of ion- exchange regeneration waste from 3.7×10^4 Bq/mL to 3.7 Bq/mL. The sorbent was also found suitable for removing ^{137}Cs from alkaline reprocessing waste containing a high concentration of sodium salts [145].

There is now enormous literature available to the ion-exchanger practitioner on the use of inorganic ion-exchangers. The literature review shows the materials used as inorganic ion-exchangers have become an established class of materials of great analytical importance. The first monograph that is also of historical importance was written by *C.B. Amphlett* in 1964 [146], one of the first research workers in the development of modern inorganic sorbents who described the beginning of the rapid development of this subject. *Barrer* wrote an excellent monograph on contemporary zeolite and clay minerals. In the 1980s, the monograph of the *Clearfield et al.* made a great contribution to the understanding of the structure and mechanism of sorption processes on the acidic salts of multivalent metals and hydrous oxides [147].

Insoluble polybasic acid salts of polyvalent metals have shown a great promise in preparative reproducibility, ion-exchange behavior, and both chemical and thermal behavior. Many metals such as aluminium, antimony, bismuth, cerium, cobalt, iron, lead, niobium, tin, tantalum, titanium, thorium, tungsten, uranium and zirconium have been used for the preparation of ion-exchange materials. Also a large

number of anionic species such as phosphates, tungstate, molybdate, arsenate, antimonate, silicate, telluride, ferrocyanide, vanadate, arsenophosphate, arsenotungstate, arsenomolybdate, arsenosilicate, arsenovanadate, phosphotungstate, phosphomolybdate, phosphosilicate, phosphovanadate, molybdosilicate and vanadosilicate *etc.* have been used to prepare inorganic ion-exchangers. The majority of works carried out on zirconium, titanium, tin, niobium and tantalum. The literature survey reveals that a good volume of work has been carried out on single as well as three components (salts of heteropolyacids) inorganic ion-exchangers of both amorphous and crystalline nature. Inorganic ion-exchangers of double salts, based on tetravalent metal acid (TMA) salts often exhibit much better ion-exchange behavior as compared with single salts [147]. A comprehensive literature survey of various inorganic ion-exchange materials based on Tin(IV) and Th(V) prepared so far and their salient features [148-216] with their selectivities are summarized in Table 1.1. *Varshney and Khan* have published their findings on arsenophosphate [172], arsenosilicate [188], hexacyanoferrate(II) [197] of tin(IV), amine and silica based tin(IV) hexacyanoferrate(II) [197,198] and arsenophosphate [217], silicate and phosphate [218] of antimony(V) cation-exchangers. Different phases of these ion-exchangers have been found selective for K^+, Cd^{2+}, Zr^{4+} and Th^{4+} and some kinetic and thermodynamic parameters for M^{2+}-H^+exchanges have also been investigated on these cation-exchangers [219-225].

Table 1.1

List of various inorganic ion-exchange materials based on Tin(IV) and Th(V) prepared so far and their salient features

S. No.	Material	Nature	Composition	Empirical formula	Selectivity	Refer-ences
(I) Tin based exchangers						
1	Stannic phosphate	Amorphous	P:Sn =1.25 - 1.50	SnO_2. $0.62P_2O_5$. nH_2O	Na(I), Li(I), K(I), Rb(I), Cs(I), Cu(II), Zn(II), Ni(II), Co(II)	[148] [149]
		Crystalline	---	$SnO_2.P_2O_5$. $2H_2O$	Zr(IV)	[150,151]
2	Stannic tungsto-phosphate	---	Sn:W:P 2:1: 3.2	---	---	[152]
3	Stannic EDTA	Amorphous	---	---	---	[153]
4	Stannic molybdo-phosphate	---	Sn:Mo:P 1:0.33:2.0	---	---	[154]
		Semi-crystalline	Sn:Mo:P= 40:26.5:0.7	----	Cs^+, Sr^{2+}	[155]
5	Tin oxide (hydrated)	Amorphous	---	---	$[Fe(CN)_6]^{4+}$, $[Fe(CN)_6]^{3+}$-SCN^-	[156]
6	Stannic arsenate	Amorphous	Sn/As = 1.84	---	Pb(II), Fe(III), Al(III), Ga(III), In(III)	[157] [158]
		Crystalline	---	$SnO_2.As_2O_5$. $2H_2O$	Li(I), Na(I), K(I)	[159]
7	Stannic antimonate	Amorphous	Sb/Sn = 1.0	$SnO_2.Sb_2O_5$. nH_2O	Cu(II), Ni(II), Co(II)	[160,161]
8	Stannic molybdate	Amorphous	Sn/Mo = 1.0	---	Pb(II)	[162]
9	Stannic selenite	Amorphous	Sn/Se = 1.33 Sn/Se = 1.0	$[(SnO_4)(OH)_2$ $(SeO_3)_3$. $6H_2O]$	Li(I), Na(I), K(I), Cu(II), Fe(III),Sc(III), La(III)	[163]

10	Stannic tungstate	Amorphous	Sn/W = 1.33	---	Co(II), Ba(II), Ni(II), Pb(II), Mn(II),Cu(II), Sr(II)	[1164]
11	Stannic vanadate	Amorphous	Sn/V = 1.0	$[(Sn(OH)_3 V_3O_9. 4H_2O]_n$	K(I),Na(I), Li(I)	[165]
12	Stannic vanado pyrophos-phate	Micro - crystalline	---	---	Ag(I), Cu(II), Pb(II), Bi(III), Zr(IV)	[166]
13	Stannic ferro-cyanide	Amorphous	Sn/Fe = 3.0	$[(SnO)_3(OH)_3. HFe(CN). 3H_2O]_n$	K(I), Ba(II), Na(I)	[167]
14	Stannic silicate	---	---	---	---	[168]
15	Stannic hexa-metaphos-phate	---	---	---	Ag(I), Pb(II)	[169]
16	Stannous ferro-cyanide	Amorphous	Sn/Fe = 1.0	$[SnO.H_4Fe(CN)_6. 2.5H_2O]_n$	Cu(II), Ni(II), Mg(II), Mn(II), Y(III)	[170,171]
17	Stannic arseno-phosphate	Amorphous	Sn:As:P 1:1:1	$(SnO_2)_5. (H_3PO_4)_3 (H_3AsO_4). nH_2O$	Th(IV), Zr(IV), K(I)	[172,173]
		Crystalline	---	$Sn(HAsO_4)(HPO_4). H_2O$	---	
18	Stannic molybdo arsenate	Amorphous	Sn:Mo:As 2:1:1	---	---	[174]
19	Stannic pyrophos-phate	Amorphous	$Sn:PO_4^{3-}$ 1:2	---	Zr(IV), Th(IV), Y(III), Bi(III)	[175]
20	Stannic sulfide	Amorphous	---	---	Cu(II)	[176]
21	Stannic phospho-silicate	Amorphous	Sn:Si:P 2:2:3	$(SnO_2)_2 (SiO_2)_2 (H_3PO_4). NH_2O$	Hg(II)	[177]
22	Stannic pyro-antimonate	---	---	---	---	[178]
23	Stannic seleno-phosphate	Amorphous	Sn:Se:P 1:1:1	---	---	[179]
		Crystalline	Sn:Se:P 4:1:6	$[(SnO)_4 (OH) (HSeO_3)(H_2P$	---	[180]

				$O_4)_6]_n.\ 4H_2O$		
24	Stannic seleno-pyrophos-phate	Amorphous	$Sn:Se:PO_4^{3-}$ 1:1:1	(15SnO.8OH) ($10H_2P_2O_7.O_2$ $HSeO_3$). 5n H_2O	Ag(I), Pb(II), Sr(II), Zr(IV)	[181]
25	Stannic tungsto-arsenate	Amorphous	Sn:W:As 12:5:2	---	Ba(II), Cu(II)	[182]
26	Stannic antimono-phosphate	Amorphous	---	---	Pb(II), Ce(III), Sm(III)	[183]
		Crystalline	---	---	Pb(II), Sm(III), La(III)	
27	Stannic vanado-arsenate	Amorphous	Sn:V:As 1.94:1.14:1	---	Ba(II)	[184]
28	Stannic tungsto-selenate	Crystalline	Sn:Se:W 7: 1:18	$[(SnO_2)_7.$ $HSeO_3$ $(HWO_4)_{18}.$ $45H_2O]$	Th (IV), Ce(IV)	[185]
29	Stannic vanado-phosphate	Crystalline	---	---	Ba(II), Cu(II)	[186]
30	Stannic tungsto-vanado-phosphate	Amorphous	Sn:W:V: P 1:1:1:1	---	---	[187]
31	Stannic vanado-tungstate	Amorphous	Sn:V:W 2:1:1	---	Al(III)	[186]
32	Stannic arseno-silicate	---	---	---	---	[188]
33	Tin(IV) antimonite	Amorphous	Sn:Sb = 2 :11	$Sn_2[Sb$ $(OH)_6]_{11}.$ $8H_2O$	Pb(II)	[189]
34	Tin(IV) vanado-pyrophos-phate	Amorphous	---	---	---	[190]
35	Tin(IV) sulpho-silicate	Crystalline	---	---	---	[191]
36	Stannic hexacyano Ferrate(III)	Amorphous	---	---	---	[192]

37	Stannic seleno-arsenate	Amorphous	Sn:Se:As 1:1:1.02	---	Hg (II)	[193]
		Crystalline	---	---	---	[194]
38	Stannic iodo-phosphate	---	---	---	Hg (II)	[195]
39	Stannic borato-phosphate	Amorphous	---	---	---	[196]
40	Stannic hexacyano-Ferrate(II)	---	---	---	Tl(I), Ba(II), Pb(II), Ce(IV), Th(IV)	[197]
41	Amine based stannic hexacyano-ferrate(II)	---	---	---	Cd (II), Cu(II), Hg(II)	[198]
42	Silica based stannic hexacyano-ferrate(II)	Amorphous	Sn:Fe:Si 5:4:2	---	---	[199]
43	Stannic silico-molybdate					[200]
44	Sodium stanno-silicate	------	Sn:Si= 1:1	$Na_2(SnO_2)_x(SiO_2)_y.zH_2O$	Ag(I)	[201]
45	Stannic vanado phosphate	Crystalline	Sn:V:P= 3:3:10	-------	--------	[202]

(II) Thorium based exchangers

1	Thorium phosphate	Amorphous	P/ Th = 1.9-2.1	--------	Pb(II), Fe(III), Bi(III)	[203]
		Crystalline	Th/PO_4 = 0.50	$Th(HPO_4)_2.2H_2O$	Ca(II), Sr(II), Ba(II)	[204]
		Fibrous	-------	$ThO_2.P_2O_5.2H_2O$	-------	
2	Thorium arsenate	Crystalline	As/Th =1.53	$Th(HAsO_4)_2.H_2O$	Li(I)	[205,206]
3	Thorium antimonate	Amorphous	Sb:Th =3.67 - 4.27	--------	-------	[207]
4	Thorium	Crystalline	-------	--------	Fe(III),	[208]

	molybdate				Zr(IV)	
		Amorphous	Th / Mo = 0.50	--------	Fe(III), Zr(IV), Pb(II)	[209]
5	Thorium Tungstate	Crystalline	Th/W = 2.0	$Th(OH)_2(HO_4)_2.nH_2O$	Cs(I), K(I), Na(I)	[210]
		Granular	-------	--------	--------	[211]
		Amorphous	------	--------	Bi(III), Hg(II)	[212]
6	Thorium oxide	Amorphous	------	$Th(OH)_n.nH_2O$	Na(I), Rb(I), Ca(II), Sr(II)	[213]
7	Thorium tellurite	-------	Th:Te = 1:2	--------	Pb(II), Co(II), Cu(II)	[214]
8	Thorium phosphosilicate	Amorphous	Th:P:Si=1:1.28:1.12	$(ThO_2.H_3PO_4.H_4SiO_4).6H_2O$	Hg^{2+}	[215]
9	Thorium iodate	--------	Th:I= 1:1	$ThO_2.I_2O_5.nH_2O$	--------	[216]

1.5.3.2. Organic Ion-exchange Materials

1.5.3.2.1. Natural organic ion-exchangers

A large number of organic materials exhibit ion-exchange properties; these include polysaccharides (such as cellulose, algic acid, straw and peat), proteins (such as casein, keratin and collagen) and carbonaceous materials (such as charcoals, lignites and coals). Of these, only charcoals, coal, lignite and peat are used commercially. Although they exhibit a very low ion-exchange capacity compared with synthetics, they are widely available at a very low cost. They are normally used as general sorbents, with their ion-exchange properties being a secondary consideration. Commercially available materials are often treated or stabilized with other additives to improve their uniformity or stability. Some materials, such as charcoals, can be doped with chemicals to improve their capacity or selectivity.

The main limitations of natural organic ion-exchangers are:

- Their low exchange capacity compared with other materials,
- Their excessive swelling and tendency to peptize,
- There is very limited radiation stability of cellulosic and protein materials,
- Their weak physical structures,
- Their non-uniform physical properties,
- That they are non-selective,
- That they are unstable outside a moderately neutral pH range,

1.5.3.2.2. Modified natural organic ion-exchangers

To improve exchange capacity and selectivity, some naturally occurring organic ion-exchangers are modified; for example, cellulose based cation-exchangers

may be modified by the introduction of phosphate, carbonic or other acidic functional groups. The sorption parameters of natural materials can be modified by a chemical and/or thermal treatment; for example, by treating clinoptilolite with a dilute solution of acids or some salts, a more selective form of sorbent can be developed for a particular radionuclide [226].

1.5.3.2.3. Synthetic organic ion-exchangers

The largest groups of ion-exchangers available today are synthetic organic resins in a powdered (5–150 μm) or bead (0.5–2 mm diameter) form. The framework, or matrix, of the resins is a flexible random network of hydrocarbon chains. This matrix carries the ionic groups such as: - SO_3^-, - COO^-, - PO_3^{2-}, - AsO_3^{2-} *etc.* in cation-exchangers, and - NH_3^+, - NH_2^+, - N^+, - S^+ etc. in anion-exchangers. Ion-exchange resins thus are cross-linked polyelectrolytes. The resins are made insoluble by cross-linking the various hydrocarbon chains. The degree of cross-linking determines the mesh width of the matrix, swelling ability, movement of mobile ions, hardness and mechanical durability. Highly cross-linked resins are harder, more resistant to mechanical degradation, less porous and swell less in solvents. When an organic-ion exchanger is placed in a solvent or solution it will expand or swell. The degree of swelling depends both on the characteristics of the solution/solvent and the exchanger itself and is influenced by a number of conditions, **such as:**

- The solvent's polarity,
- The degree of cross-linking,
- The exchange capacity,
- A strong or weak solvation tendency of the fixed ionic groups,

- The size and extent of the solvation of counter ions,
- The concentration of the external solution,
- The extent of the ionic dissociation of functional groups,

The main advantages of synthetic organic ion-exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic media. The main limitations are their limited radiation and thermal stabilities. At a total absorbed radiation dose of 10^9 to 10^{10} rads most organic resins will exhibit a severe reduction in their ion exchange capacity (a 10 to 100% capacity loss), owing to physical degradation at both the molecular and macroscopic level. Cation-exchange resins are generally limited to operational temperatures below about 150 °C, while anion-exchange resins are usually limited to less than 70 ^{0}C. This requires that some streams, such as reactor coolant water, be precooled substantially before their introduction to the ion-exchange media. A general comparison of organic and inorganic ion-exchanger is given in Table 1.2.

1.5.3.3. Chelating ion-exchange materials

The use of ligand or complexing agent in solution in order to enhance the efficiency of separation of cation mixtures (*e.g.* lanthanide) using conventional cation or anion-exchange resins is well established. An alternative mode of application of complex formation is, however, the use of chelating resins that are ion-exchangers in which various chelating groups (*e.g.* dimethylglyoxime, iminoacetic acid *etc.*) have been incorporated and are attached to the resin matrix. Thus, a chelating ion-exchange resin consists of essentially of two components, i.e., a chelating group and

Table 1.2

General comparison of organic and inorganic ion-exchangers

Properties	Organic exchangers	Inorganic exchangers	Comments
Thermal stability	Fair to poor	Good	Inorganics are especially good for long term stability
Chemical stability	Good	Fair to good	Specific organics and inorganics are available for any given pH range
Radiation stability	Fair to poor	Good	Organics are very poor in combination with high temperatures and oxygen
Exchange capacity	High	Low to high	The exchange capacity will be a function of the nature of the ion being removed, its chemical environment and the experimental conditions
Selectivity	Available	Available	For some applications, such as cesium removal, inorganics can be much better than organics, owing to their greater selectivity Ion selective media are available in both organic and inorganic forms
Regeneration	Good	Uncertain	Most inorganics are sorption based, which limits regeneration
Mechanical strength	Good	Variable	Inorganics may be brittle or soft or may break down outside a limited pH range
Cost	Medium to high	Low to high	The more common inorganics are less costly than organics
Availability	Good	Good	Both types are available from a number of commercial sources
Immobilization	Good	Good	Inorganics can be converted to equivalent mineral structures, organics can be immobilized in a variety of matrices or can be incinerated
Handling	Good	Fair	Organics are generally tough spheres, inorganics may be brittle; angular particles are more friable
Ease of use	Good	Good	If available in a granulated form both types are easy to use in batch or column applications

a polymeric matrix. Therefore, the properties of both components have to be taken in to account when designing and synthesizing a chelating ion-exchange resin. Several workers postulated criteria for a compound to act as a selective chelating ion exchanger. These are summarized as:

1. The chelating ligand attached to a solid matrix should possess strong binding properties and selectivity towards certain metal ions.
2. The chelating group should be capable of undergoing incorporation in a polymeric matrix and allow the process of polymerization or resinfication; in turn, the chelating polymer should be resistant to strong acids and alkalies at elevated temperature.
3. The chelating ligand should preferably be multidentate, permitting formation of a 1:1 or 1:2 chelate with a metal ion.
4. The chelating ion-exchanger should possess good swelling properties and compatibility between the polymer and the medium (generally aqueous) is essential; this can be regulated by the presence of hydrophilic groups on the polymer and by the extent of cross-linking.
5. Both arms of a chelate structure should be present on the monomer unit in proper special configuration.
6. The chelating agent must possess sufficient stability, so that the functional structure is not changed by polymerization during the synthesis of the resin.
7. It should be capable to substitution into a polymeric matrix and should be compact enough so that its chelating ability is not hindered by the dense polymeric matrix.

A chelating resin with desired selectivity can be prepared by applying these conditions. According to these conventional approaches chelating ion-exchangers have been extensively studied and modified synthetic materials such as cellulose [227,228], polystyrene [229], divinylbenzene [230], hydrazine-modified polyacrylonitrile [231], modified agricultural residues [232] and starch [233] have been also been demonstrated as efficient chelating adsorbents for heavy metal removal. Recently, *Orlando et al.* [234] have prepared modified chelating ion exchangers from bagasse (BC) by microwave radiation through reaction with reagents that contain chelating functional groups, such as thiourea, urea, melamine, polyethyleneimine, ethylenediamine, diethylenetriamine, iminodiacetic acid and glycine, and their resultant performance in removing mercury(II) from aqueous solution.

Chelating resins containing aminophosphonate [235], dithiocarbamate [236], hexylthioglycolate [237], iminodiacetate [238], isothiouronium [239], poly (ethylenemercaptoacetamide) [240], thioacetamide [241], thiol [242,243] and thiosemicarbazide [244] are also generally employed for heavy metal sorption. Examples of various chelating groups and their application for selective preconcentration of inorganic elements have been reviewed by *Kantipuly et al.* [245]. Diphonix resin containing both sulphonic and *gem*-diphosphonic acid groups exhibited a high affinity for extraction of actinide ions [246-248]. The removal of uranium, cadmium and chromium from phosphoric acid solutions using chelating resins has been reported by *Kabay et al.* [249,250]. Ion-exchange and chelating resins

were the subject of many reviews [251-253]. Among various types of ion-exchangers with acidic ligands those having phosphonate functionality are of particular interest since they are selective towards heavy metal cations [254-256]. Development of this type of ion-exchangers started in the late 1940s [257] with phosphorylation of poly(vinyl alcohol) using various phosphorylating agents. Next, were reports on introducing phosphonic [258] and phosphinic [259] functionality to styrene/divinylbenzene and to its chloromethyl derivative. This type of modification was also presented in ref. [260], where more attention was paid to the type of polymeric matrix and in ref. [261,262], where ion-exchange/complexing properties of phosphinic and phosphonic resins in the form of acid, monoester and diester were presented. Other types of phosphonic functionality immobilized on insoluble polymeric matrices include methylenediphosphonate [263] and ethylenediphosphonate carboxyethyl phosphonate [264] immobilized on vinylbenzyl chloride/divinylbenzene copolymers. The latter one contained also a carboxylate group as part of the ligand and the same situation pertained in the case of 1,1-dicarboxylate-2-ethanephosphonate and 1,1-diphosphonate-2-ethanecarboxylate immobilized on vinylbenzyl chloride/styrene/divinylbenzene copolymer [265]. In all cases resins displayed good selectivity towards multifunctional cations. The resin with phosphonate groups in the geminal position retained its ion-exchange/coordinating properties even at very low pH [263], whereas ethylenediphosphonate and carboxyl containing resins, being less acidic, more selective at pH 1–2. α-zirconium phosphonates chelating legand with

phosphonatomethyliminodiacetic acid was studied for the structure by *Poojary et al.* [266]. The arrangement of ZrO_6 as octahedra, PO_4 and PO_3 moieties as tetrahedra and the $N(CH_2CO_2H)_2$ group is given in Fig. 1.16. These types of chelating ion-exchangers have been developed recently and their analytical applications explored [267]. Complexions have been used for the preparation of new chelating resins for separating metal ions on the basis of complex formation [268]. A number of such ion-exchangers have been prepared by the incorporation of ligands on resins [269]. 8-hydroxy quinoline [270] sorbed on porasil is capable of separating metal ions at trace level. Eriochrome black–T modified graphite columns have been used for the separation of metal ions [271]. A PAN [1-(2-pyridylazo-2-napthol)] sorbed zinc silicate [272] has been used for the recovery of precious metal ions Pt^{4+} and Au^{3+}, and ammonium-molybdophosphate [273], have been used for the quantitative separation of Cs^+ ions. Separation and retention behavior of metal ions have been achieved on tetracycline hydrochloride coated alumina [274] and zirconium(IV) selenomolybdate [275], while tetracycline hydrochloride sorbed zirconium(IV) tungstophosphate chelating exchanger has been employed in the separation of La^{3+} ions [276]. *D.K. Singh et al.* [277] has been prepared zinc silicate bonded diethyldithiocarbamate for the separation and preconcentration of some transition metal ions. *A.C.S. Costa et al.* [278] have developed a procedure for separation and preconcentation of cadmium, copper, lead and zinc by solid-liquid extraction of their cocrystalized naphthalene dithizone chelate in saline matrices. An important feature of chelating ion-exchangers is the greater selectivity, which they offer compared with

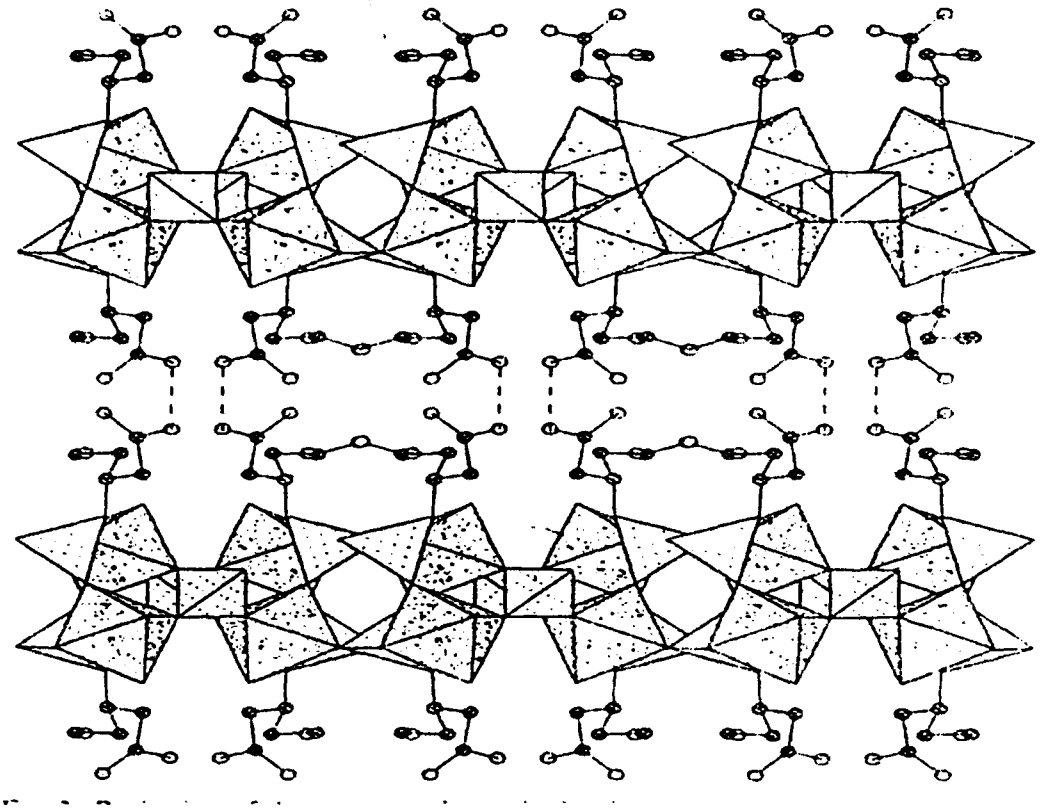


Fig. 1.16. Projection of the structure down the b axis showing the layer arrangement. The sketch depicts ZrO_6 as octahedral PO_4 and PO_3 moieties as tetrahedral and the $N(CH_2CO_2H)_2$ group and the hydrogen bonding (---).

the conventional type of ion-exchanger. The affinity of a particular metal ion for a certain chelating resin depends mainly on the nature of the chelating group. And the selectivity behavior of the resin is largely based on the different stabilities of the metal complexes formed on the resin under the various pH conditions.

1.5.3.4. Intercalation ion-exchangers

After the development of various types of inorganic ion-exchange materials, lately much interest has been developed in the study of pillared inorganic materials and intercalation compounds (new porous intercalates) that can be synthesized by introducing some organic molecules in the matrix of layered inorganic ion-exchangers (Fig. 1.17). However, the intercalating properties were first discovered in 1965 by *Michel* and *Weiss* [279,280]. Upto 1975 no paper was published on this subject, after that, the intercalation behavior of layered insoluble acid salts of tetravalent metals was written by *Lagaly et al.* [281]. The main advantage of a pillared structure is that it allows ready access of large ions and complexes to the interior due to the increase in the inter layer distances and pore sizes as shown in Fig. 1.18. This is very useful in radioactive waste cleanup. Amongst the new developments of ion exchangers, intercalation compounds have played an important role in the field of separation science and technology. These compounds can be synthesized by introducing some organic ions or molecules in the matrix of inorganic ion exchangers. Alumina, kaolin, clays, bentonite, pectin, alginic acid *etc.* have been used as adsorbent with stimulated considerable interest in medical science throughout world. Hence, intercalation is a process in which neutral polar molecules are inserted

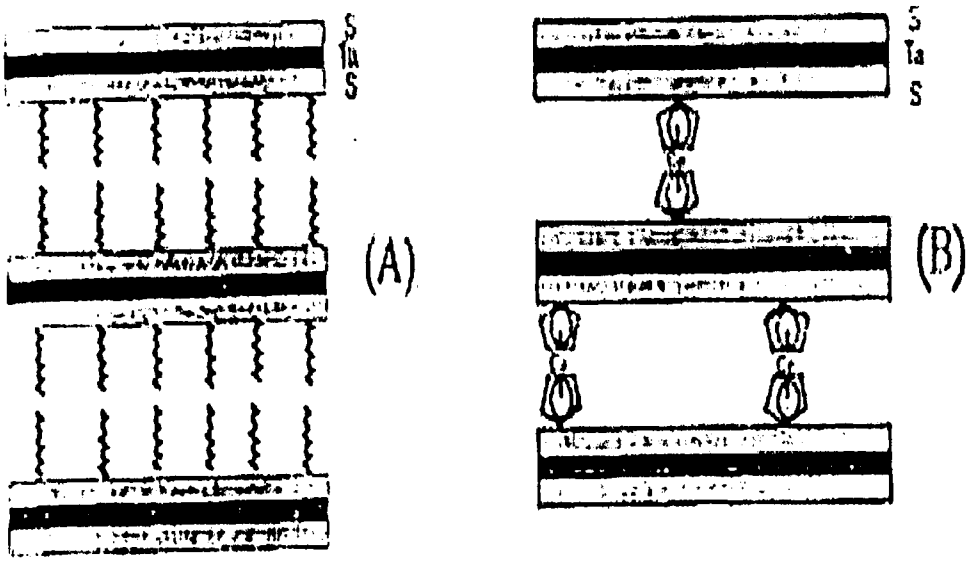


Fig. 1.17. Intercalation compounds (A) Long chain amine intercalate of a metal disulfide (B) Cobaltocene intercalated in TaS_2.

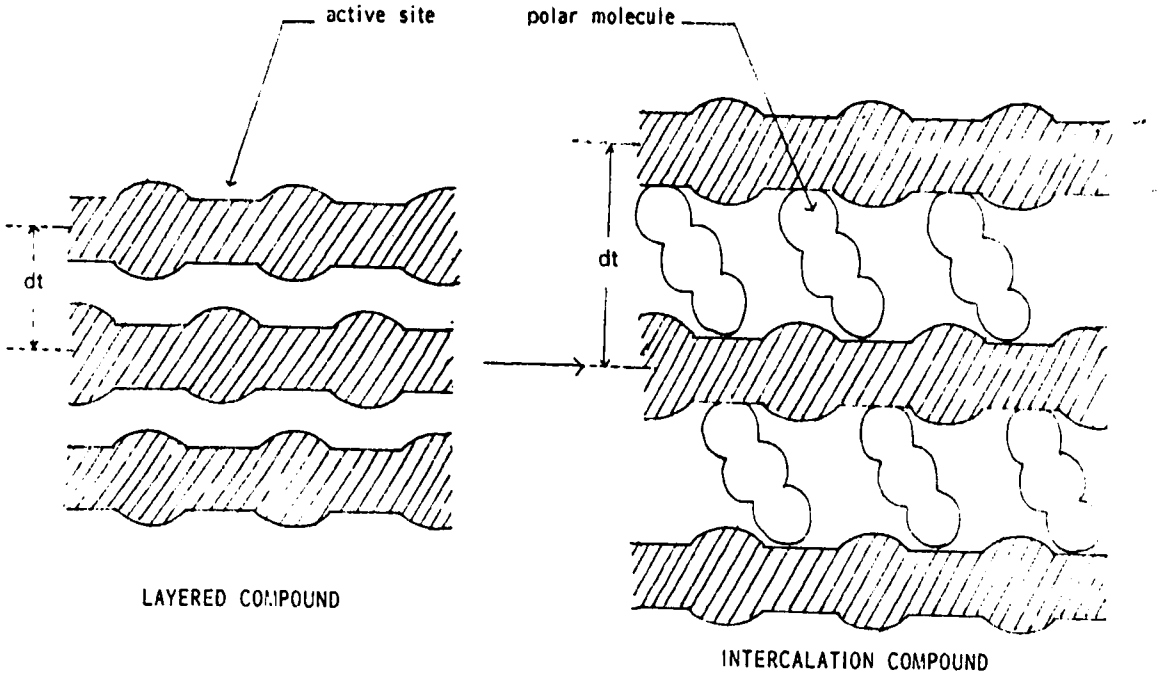
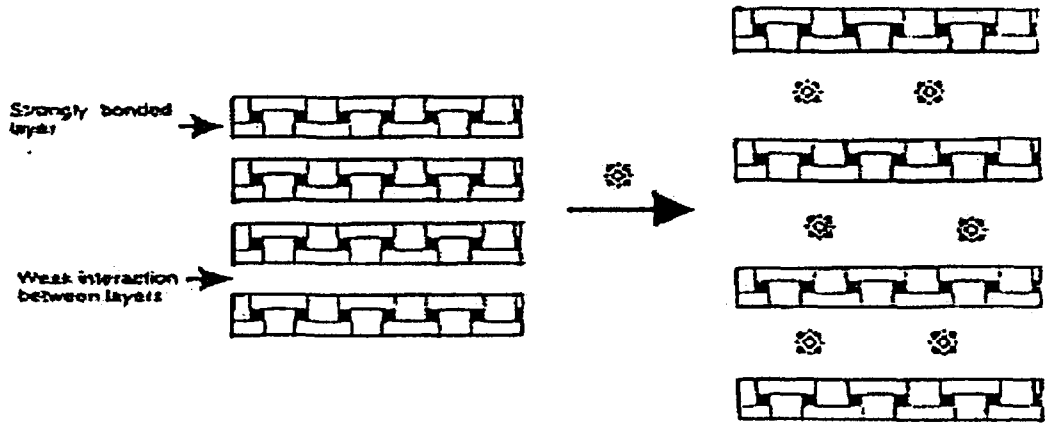


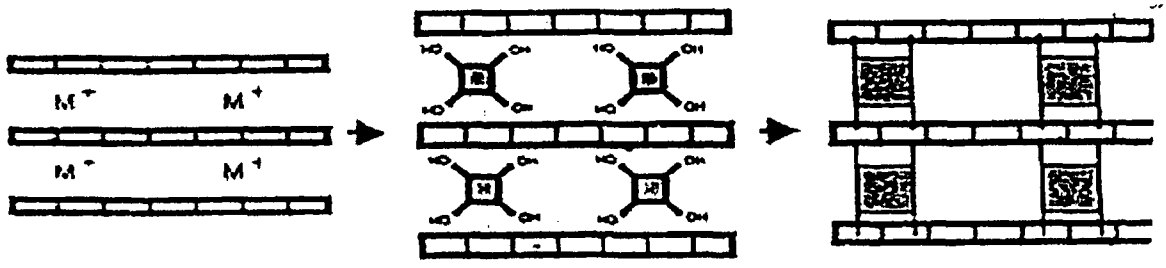
Fig. 1.18. Schematic illustration of the intercalation of polar molecules.

between the sheets of a layered insoluble compound (Fig. 1.19). Layered inorganic ion-exchangers with a non rigid structure such as the acid phosphates of tetravalent metals ($Me(IV)(HPO_4)_2 \cdot nH_2O$; Me = Zr, Ti, Sn; n=1,--------) are able to exchange transition metal ions [282] and to intercalate organic molecules [283]. Each layer consists of tetravalent atoms sandwiched between tetrahedral phosphate or arsenate group [284-288]. The gamma phases of zirconium phosphate, γ-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$, (γ-ZrP) and titanium phosphate, γ-$Ti(PO_4)(H_2PO_4)\cdot 2H_2O$, (γ-TiP) may be considered among the most studied inorganic ion-exchange materials with a layered structure [289,290]. The organic diamine 2,9-dimethyl-1,10-phenanthroline (dmp) is able to be intercalated between the layers of γ-ZrP and γ-TiP to give the intercalated phases denoted as γ-ZrPdmp and γ-TiPdmp [291]. These materials subsequently exchange copper ions giving dmpCu complex formed in situ (γ-ZrPdmpCu and γ-TiPdmpCu) (Fig. 1.20).

Alberti et al. [292] have reported the synthesis and characterization of a new type of zirconium phosphate such as zirconium phosphate hemihydrate [α-$Zr(HPO_4)_{0.5}\cdot H_2O$]. A large number of other new materials have also been prepared on zirconium phosphate by pillaring methods. *Alberti* and *coworkers* [293] have intercalated α-$Zr(IV)(RPO_3)_2.H_2O$ by phenyl containing $-SO_3H$ groups and γ-$Zr(IV)(PO_4)(H_2PO_4).2H_2O$ by crown ether. *U. Costantino* [294] has given a detailed description of intercalation of alkanols and glycols into α-$Zr(HPO_4).H_20$ and also developed zirconium phosphate-phosphite [295]. *Clearfield* and *Tindwa* [296] have studied in detail the uptake of *n*- phenylamine, *n*- butyl amine and ethylene diamine



(I)



(II)

Fig. 1.19. Schematic of (I) An intercalation reaction and (II) Pillaring in clays.

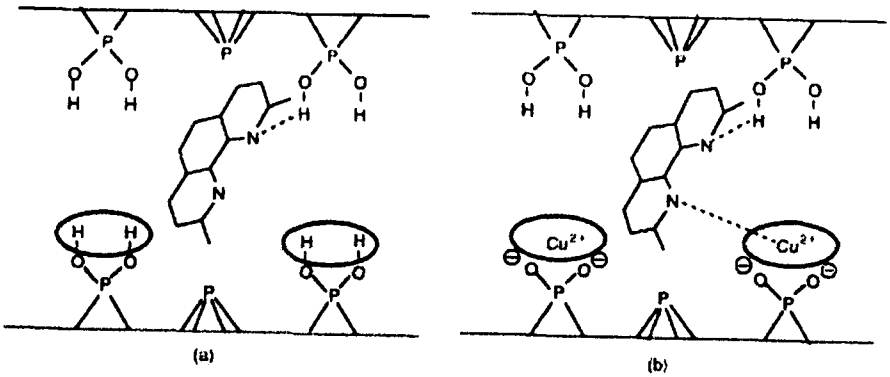


Fig. 1.20. Possible arrangements of dmp (a) and dmpCu complex (b) between the layers of the γ-ZrP exchanger.

on α-$Zr(HPO_4)_2.H_2O$. *Dines et al.* [297] have prepared monophenyl, diphenyl and triphenyl bridging pillared zirconium phosphates by using phenyl disulphonic acids to bridge across the layers. They have also shown that it is possible to form three – dimensional or pillared analogous of the phosphonates by utilizing α, ω - diphosphonic acids. *Varshney et al., Rawat et al., Singh et al.* and *Qureshi et al.* have also studied on amine tin(II) hexacyanoferrate(II) [298], tin(IV) diethanol amine [299], iron(III) diethanol amine [300] and zirconium(IV) ethylene diamine [301], respectively.

Recently, some intercalation ion-exchangers have been developed and reported in the literature. *Hudson et al.* [302] have reported the intercalation of monoamine into α-$Sn(HPO_4)_2.H_2O$ and investigated the ion-exchange behavior of amine in the presence of transition metal ions. *Wang et al.* have reported the selective separation of Cs^+ on zirconium phenyl diphosphonate phosphate [303]. *Malik et al.* [304] have reported pyridinium tungstoarsenate, selective for Rb^+ and Cs^+ and *Singh et al.* intercalated aniline into tin(IV) phosphate [305] and Zr(IV) phosphate, $[(ZrO_2)_2.(C_6H_5NH_2)HPO_3.\ 3.7H_2O]$; selective for Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} [306]. *Nabi et al.* have reported the synthesis, characterization and analytical applications of Zr(IV) sulfosalicylate [307] (selective for Ag^+ and Hg^{2+}) and pyridinium-tin(IV) tungstoselenate [308].

1.5.3.5. 'Organic-inorganic' composite ion-exchange materials

The conversion of inorganic ion-exchange materials has been taking place into composite ion-exchange materials is the latest development in this discipline. Sol-gel

derived composite materials have found numerous applications in the areas of chemistry, biochemistry, engineering, and material science [309,310]. The 'organic-inorganic' hybrid materials prepared via the sol-gel technique have attracted significant attention in the literature [311] and the materials as ion-exchangers prepared by this technique were also described. The combination of organic and inorganic precursors yields hybrid materials that have mechanical properties not present in the pure materials. Often, strain built up during drying and heat treatment (densification) results in cracking of the materials. To diminish this strain, the material can be made more compliant by the introduction of organic groups. The organic group can be reactive, which implies that it is able to form an organic network as well as an inorganic network. In this case, the organic group is classified as network builder. Another preparation of the composite ion-exchangers has been carried out with the binding of electrically conducting organic polymers, *i.e.* polyaniline, polythiophene and polypyrrole *etc.*

These polymers based composite ion-exchange materials show the improvement in a number of its properties. One of them is the improvement in its granulometric properties that makes more suitable for the application in column operations. In some of the cases, it is observed that increase in the number of cycles without affecting its ion-exchange capacity as well as ion-exchange equilibria. The binding of organic polymer also introduces the better mechanical properties in the end product, *i.e.* composite ion-exchange materials.

More recently, some organic-inorganic composite ion-exchange materials

have been developed in these laboratories. *Khan et al.* have reported polypyrrole Th(IV) phosphate [312], polyaniline Sn(IV) phosphate [313] (tentative structures are shown in Fig. 1.21 and 1.22), polypyrrole/polyantimonic acid composite system [314], polyaniline Sn(IV) tungstoarsenate [315], polyaniline Sn(IV) arsenophosphate [316], poly-o-toluidine Th(IV) phosphate [317], nylon-6,6, Zr(IV) phosphate [318], and polystyrene Zr(IV) tungstophosphate [319] and used for the selective separation of heavy metal ions. The ion-exchange kinetics of M^{2+}-H^{+} exchange [320-324] and adsorption of pesticide [325,326] have also been carried out on these materials. *Beena Pandit et al.* have synthesized such type of ion-exchange materials, i.e. o-chlorophenol Zr(IV) tungstate and p-chlorophenol Zr(IV) tungstate [327]. *Chudasama et al.* [328] synthesized a new inorganic-organic ion exchanger by anchoring p-chlorophenol to $Zn(WO_4)_2$ and reported the material has a good ion-exchange capacity and stability.

Styrene supported Zr(IV) phosphate [329] and Zr(IV) tungstophosphate [319] hybrid material and fibrous ion-exchange materials such as polymethyl methacrylate, polyacrylonitrile, styrene, pectin and acrylamide based Ce(IV) phosphate, Th(IV) phosphate, Zr(IV) phosphate and tin(IV) phosphate [330-337] having a great analytical applications, have been investigated by *Varshney et al.* These materials can be used as ion-exchanger membranes and electrodes. Polyacrylonitrle fibers and zeolites composites have also been reported in literature. Polyaniline Zr(IV) tungstophosphate has been synthesized by *Gupta et al.* [338], which was used for the selective separation of La^{3+} and UO_2^{2+}. *Chanda et al.* reported polyacrylic acid

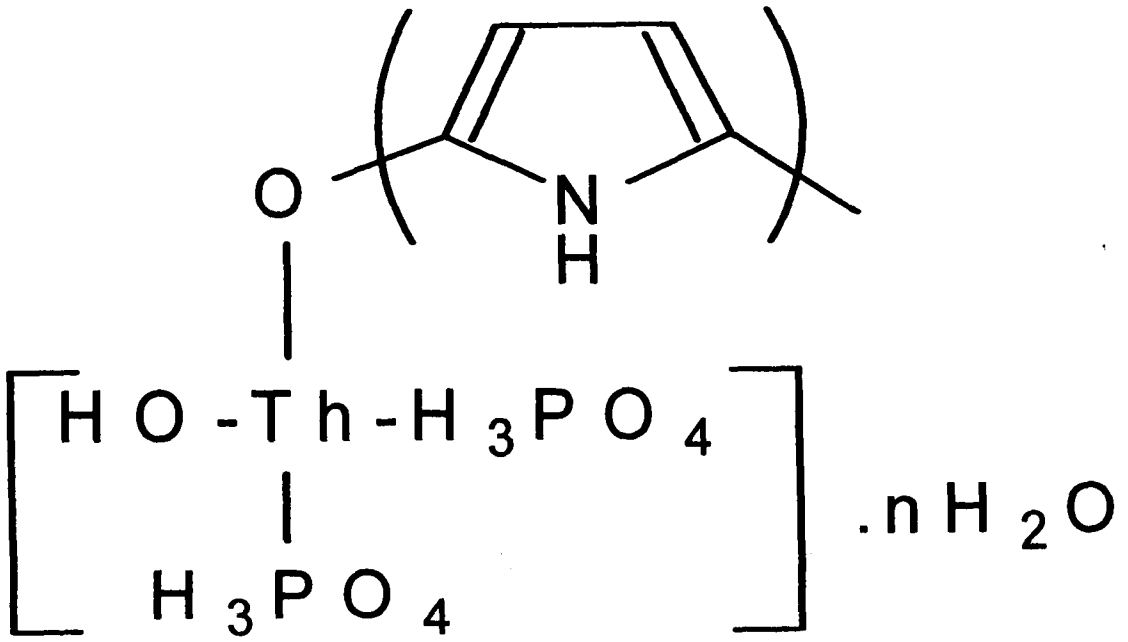


Fig. 1.21. Tentative structure of polypyrrole Th(IV) phosphate organic-inorganic composite cation-exchanger.

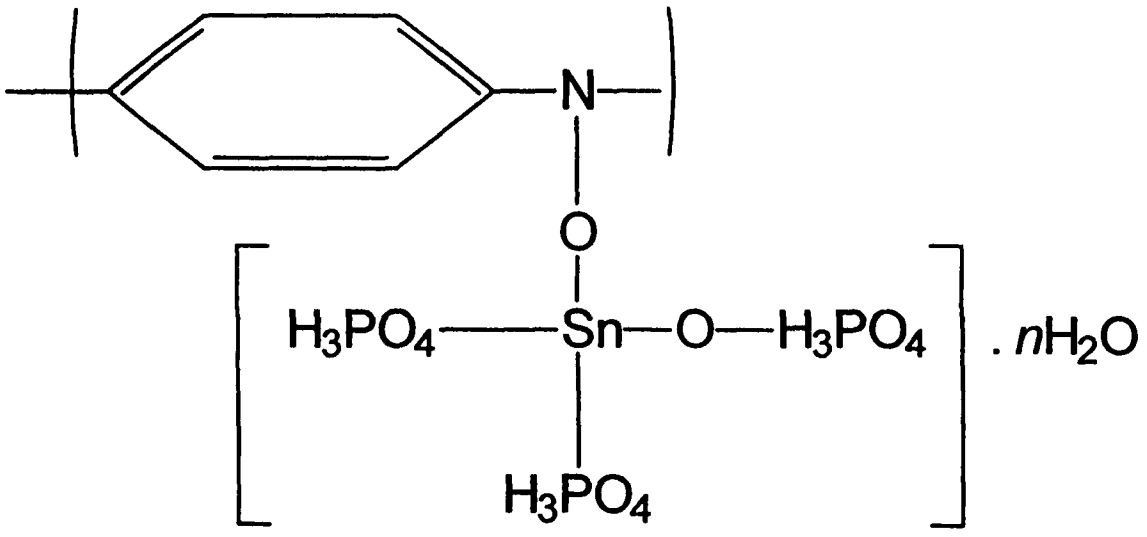


Fig. 1.22. Tentative structure of polyaniline Sn(IV) phosphate organic-inorganic composite cation-exchanger.

coated SiO_2 as a new ion-exchange material. *C.A Borgo et al.* [339] have studied ion-exchange properties and equlibrium constant of Li^+, Na^+, and K^+, on zirconium phosphate highly dispersed on a cellulose acetate fiber surface. *S.K. Tiwari et al.* [340] reported the thermolytic degradation behavior of inorganic ion-exchanger incorporated perfluro-sulphonate ionomer membrane (nafion-117).

1.5.4. Applications of Ion-exchange Materials

Ion-exchangers find applications in a wide variety of industrial, domestic, governmental and laboratory operations. The composite ion-exchangers show some better granulometric properties that facilitates its stability in column operations especially for separation, filtration and preconcentration of ionic species. The column operation suitability makes it more convenient in regeneration of exhausted beds also. These hybrid ion-exchangers having good ion-exchange capacity, higher stabilities, reproducibility and selectivity for specific heavy metal ions indicating its useful environmental applications. As in general these materials have their applications in following disciplines:

- Water softening [99,341]
- Separation and preconcentration of metal ions [342]
- Nuclear separations [343]
- Nuclear medicine [344]
- Synthesis of organic pharmaceutical compounds [345]
- Catalysis [346]
- Redox systems [347]

- Electrodialysis [348]
- Hydrometallurgy [349]
- Effluent treatment [350]
- Ion-exchange membranes
- Chemical and biosensors
- Ion memory effect [351]
- Ion-exchange fibers [352-354]
- Ion-selective electrodes [314,315,355-357]
- Proton conductors [358,359]

1.6. Electrical Properties of Materials

Consideration of the electrical properties of materials is often important when materials selection and processing decisions are being made during the design of a component or structure. The electrical behaviors of the various materials are diverse. Some need to be highly electrically conductive, whereas electrical insulativity is required of others. In order to explore the electrical properties of materials, that is, their responses to an applied electric field, it is necessary to discuss the phenomenon of electrical conduction: the parameters by which it is expressed, the mechanism of conduction by electrons, and how the electron energy band structure of a material influences its ability to conduct. These principles are extended to metals, semiconductors, and insulators. Nowadays, particular attention is given to the characteristics of semiconductors.

1.6.1. Electrical conduction in materials

Electrical conductivity σ is used to specify the electrical character of a material. It is simply the reciprocal of the resistivity, or

$$\sigma = \frac{1}{\rho} \qquad \ldots\ldots 1.4$$

and is indicative of the ease with which a material is capable of conducting an electric current. Materials show electrical conduction due to the movement of charge carriers on application of voltage as given by the basic equation -

$$\sigma = q\, n\, \mu \qquad \ldots\ldots 1.5$$

where σ is electrical conductivity of material, n is the number of charge carriers, q is

the charge and μ is drift mobility of charge carriers. Drift mobility characterizes the ease with which the charge carriers can move under the influence of applied electrical field. There are several carriers that contribute to the conductivity of the materials. Electrons and holes in the electronic conductors and cations and anions in ionic conductors.

Mechanisms that have been employed to explain the electrical conduction in materials, include ionic conduction, band type conduction, hopping and excitonic conduction, quantum mechanical tunneling between metallic domains *etc.*

1.6.2. Electrically conducting materials

The ability of materials to conduct electricity varies widely allowing their classification into good conductors (metals), semiconductors and non-conductors (insulators). Another classification of solids may be based upon the number of current carriers (electrons). A conductor has a large number of current carriers and this number is independent of temperature. An *insulator* has relatively few numbers of current carriers at ordinary temperatures and a semiconductor has current carriers, the number of which in a particular material depends on the temperature.

We already know that electrical conductivity is one of the most important properties of *metals*. Silver has the highest electrical conductivity. Copper comes next and is similar to silver from the point of view of atomic structure. Aluminium, which is light and has a high conductivity, is rapidly becoming more important as a conductor material. Gold which has conductivity higher than that of aluminium but lower than that of silver or copper does not find use in electrical industry because it is expensive.

The resistivity of metallic conductors at room temperature lies between 1.6×10^{-6} to 100×10^{-6} ohm cm^{-1} and that of insulators between 10^{9} to 10^{18} ohm cm^{-1}. The corresponding value for semiconductors is intermediate between those for conductors and insulators. It is the order of 0.01-50 ohm cm^{-1} at room temperature. The resistivity of *semiconductors* is considerably more sensitive to changes in temperature than is the case for metals. As a result compact temperature measuring instruments using semiconducting thermal resistors (thermistors) may be constructed. At high temperatures, the number of current carriers in a semiconductor is fairly large while at low temperatures this number is relatively small. The number of current carriers in a semiconductor however is many orders of magnitude smaller than in a conductor.

***K. Onnes** first observed superconductivity* in 1911; on cooling a sample of mercury below 4.2 K the resistivity of the metal suddenly decreased to an immeasurably small value. Since then many metals and their alloys, many compounds have been found which have zero resistance below a certain critical temperature; T_c. Electrical conductivities of various elements, compounds and polymers are shown in Fig. 1.23.

1.6.3. Electrically conducting polymers

Polymers have traditionally been utilized in electrical and electronic applications in view of high resistivity (their electrical conductivity lies in the range of 10^{-11} to 10^{-18} Scm^{-1}) and excellent dielectric properties. Research and development have demonstrated the possibility of obtaining polymers with almost properties

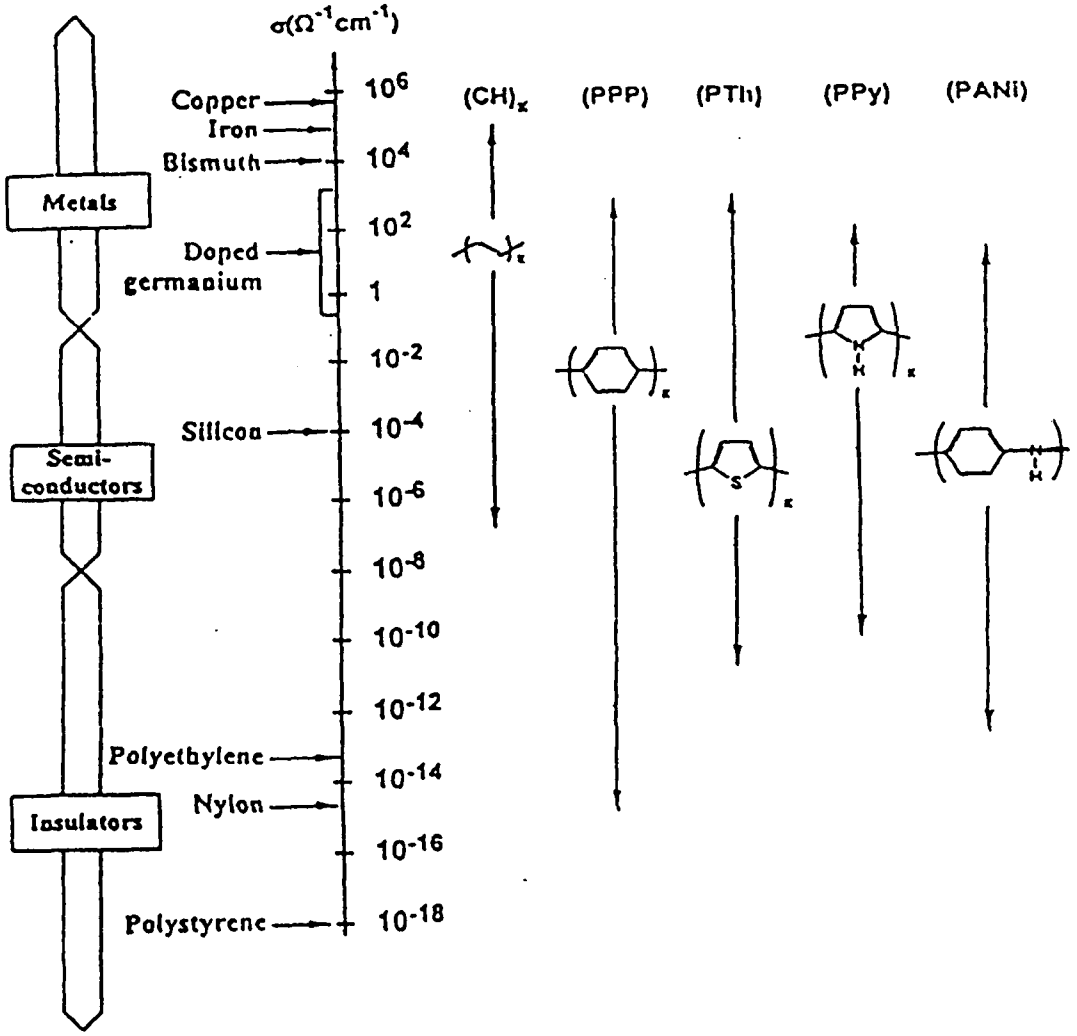


Fig. 1.23. Conductivities of main electrically conducting polymers with other classical conductors, semiconductors, and insulators

typical of any structural material, semiconductor or metal. However, due to the electrical insulating properties, polymers remain unsuccessful in replacing metals and semiconductors in electrical and electronic applications. To improve gas sensors characteristics, novel sensitive organic layers, electronic conducting polymers were developed. Now the electrically conducting polymers are establishing their place as the central constituents of various electronic and photonic systems. The award of the Noble Prize has recognized the interest of these materials for the year 2000 in Chemistry to *Heeger* [360], *MacDiarmid* [361] and *H. Shirakawa*, who synthesized the first conducting polymers and proved their potentialities in a large number of applications. The first account of observation of the electrical conductivity was reported in 1800s when it was seen that by incorporation of carbon black, the conductivity of natural rubber could be enhanced. The combination of electronic and optical properties of the semiconductors with the mechanical properties and the processibility of the polymers makes conjugated polymers rather unique and potentially useful for a wide array of applications. Conjugated polymers such as polyacetylene, polyphenylene, polythiophene, polypyrrole, polyaniline *etc.* possess a backbone that can produce, sustain and assist the motion of charge carriers in the form of electrons or holes (Fig. 1.24).

1.6.3.1. Polyaniline

In recent years, polyaniline has attracted much attention [362-364] on account of its ability, under certain conditions, to exhibit a high level of electrical conductivity [365] having potential applications such as in the fabrication of novel

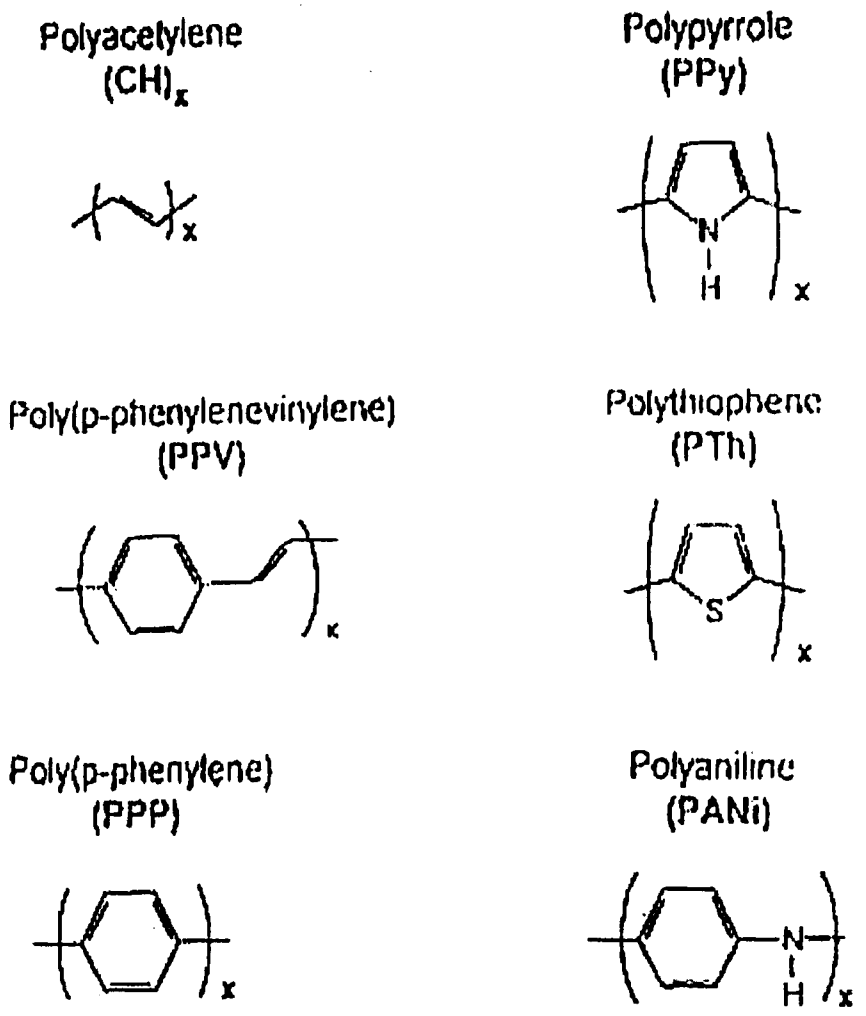


Fig. 1.24. Bond-alternate backbone of the most studied electroconducting conjugated polymers (ECPs).

batteries. Although polyaniline was first produced in the nineteenth century, interest in this polymer and its derivatives did not really begin to develop until the mid-1980s. Several chemical methods exist for the preparation of polyaniline although the preferred method utilizes electrochemical polymerization. It is known to exist in a variety of forms differing in color, some of which are not electrically conducting as shown in Fig. 1.25. Under appropriate conditions the so called emaraldine base form of the polymer reacts with dilute acids to give corresponding emaraldine salts, with protonation of the nitrogen atoms. This reaction is accompanied by a 9-10 order of magnitude increase in conductivity to $1\times10^{2} - 5\times10^{2}$ S m^{-1}. Hence it can be used in aqueous electrolyte rechargeable batteries [366]. Key attractions of polyaniline are the relatively low cost of the synthetic route from aniline and the fact that it has very important features that distinguish it from other conductive polymers.

1.6.3.2. Polypyrrole

Polypyrrole have encouraged considerable research because they are a group of polymers that can be easily produced in the doped state. It can be prepared by the electro-polymerization of pyrrole and it is then obtained as highly colored dense conducting films. It can also be prepared by chemical methods. It has been one of the first polymers used in gas sensors. Conductivities of this polymer have been reported up to 10^{4} Sm^{-1} [367]. One of the principal advantages of polypyrrole over other doped polymers is its excellent thermal stability in air. It is thermally stable upto 250 °C. Although chemical analysis of polypyrrole varies with preparative conditions, elemental analyses have indicated that the pyrrole rings remain intact with each unit being connected by its α-carbons (Fig. 1.26).

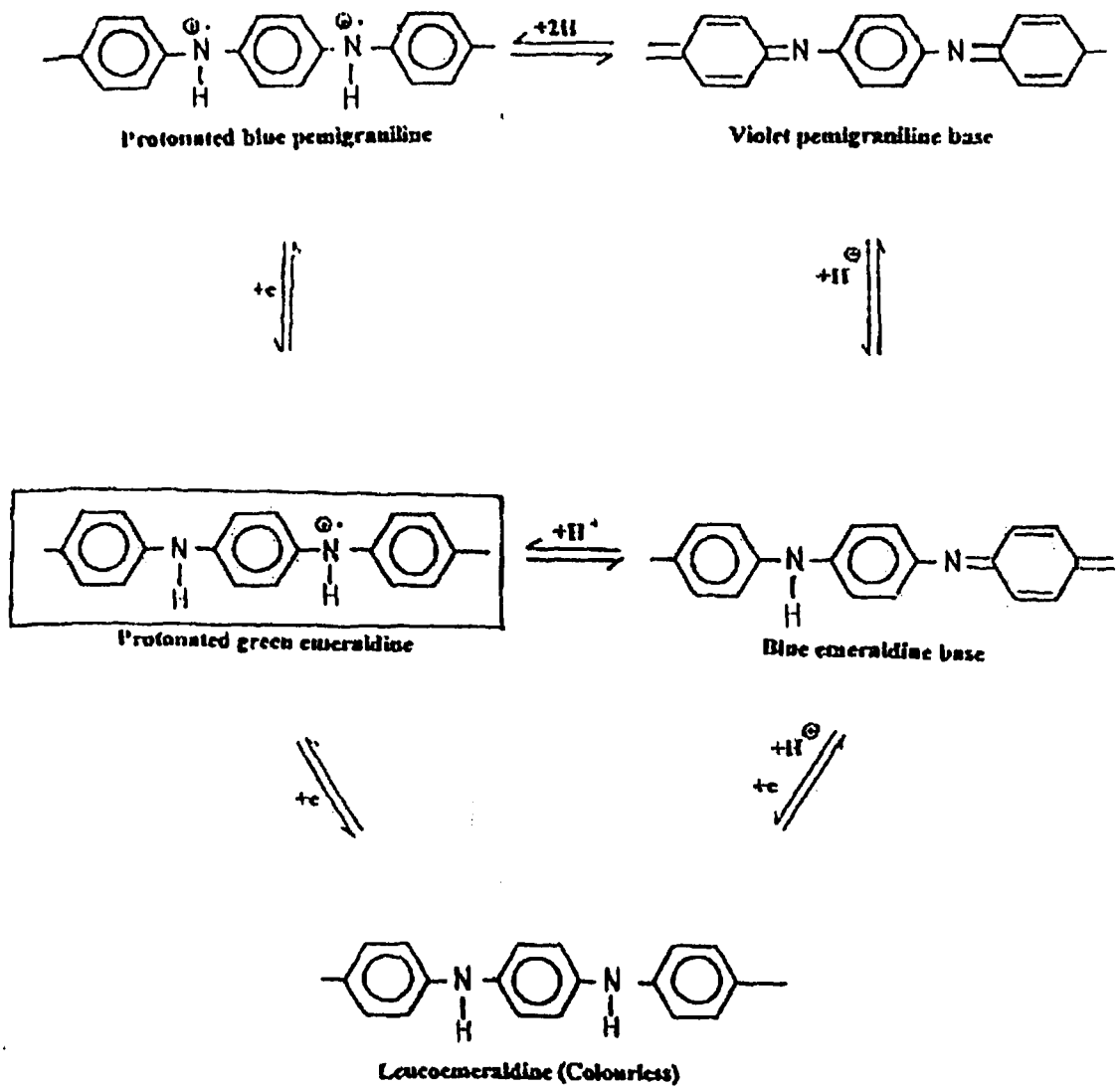


Fig. 1.25. Different forms of polyaniline.

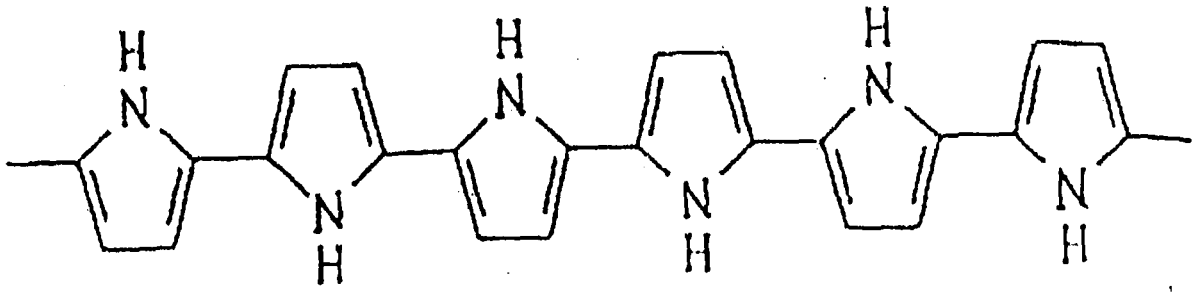


Fig.1.26. Structure of polypyrrole.

1.6.4. Electrically conducting 'organic-inorganic' composites

The conjugated backbone of electrically conducting organic polymers is responsible for their electroactive character and, therefore, possesses good tunable electrical conductivity as well as electrochromic properties [368-371]. But they are chemically sensitive and have poor mechanical properties and pose processibility problems. The inherent instability is also due to highly unsaturated backbone of conjugated polymers. Stability problems have, therefore, caused many research groups to search for conjugated polymers of high stability. To meet the demand of materials of improved performance, explosive research is going on to synthesize the composites (combinations of desirable properties of each component) of 'organic-organic' and 'organic-inorganic' nature. In the view of the above-mentioned facts, researchers have shown much interest in the study of electrically conducting behavior of 'organic-inorganic' composite materials [86,372-376]. Special interest today is focused on composite system having high conductivity at ambient and sub-ambient temperatures, since they find unique applications, such as separators in high power and rechargeable lithium batteries. Moreover, composite materials composed of oxides or polyvalent metal acid salts and conducting polymers have brought out more fields of applications, such as smart windows, toners in photocopying, conducting paints etc. [377-379].

These organic-inorganic electrically conducting composites may be prepared by mixing a conducting material in an insulating or a conducting polymer matrix. The insulating polymer matrix acts as a solid adhesive, which keeps the conducting

components together and provides mechanical strength without any contribution in electrical conduction. Thus, one or more materials (for e.g. insulating polymers, organic molecules, metal powder, inorganic compounds etc.) can be combined with electrically conducting polymer matrix to produce a new conducting material with different physical, mechanical, thermal and electrical properties. Thus, the synthesis of polymeric-inorganic composites has received a great deal of attention because it provided new materials with special mechanical, chemical, electrochemical and optical as well as magnetic properties [380-414]. Various research groups have also successfully applied conventional dispersion polymerization techniques for the preparation of sterically stabilized particles of electrically conducting polymers such as polypyrrole (Ppy) and polyaniline (PANI). The preparation of dispersions solves some problem of their limited processibility. A wide range of steric stabilizers based on various water-soluble polymers, e.g. poly(2-vinylpyridine) [415,416], poly(vinylalcohol) [417,418], poly(vinylalcohol-co-vinylacetate) [419-426], poly(oxyethylene) [427-429], poly(N-vinylpyrrolidone) [421,422,430,431], poly(vinyl methyl ether) [432-434], proteins [435] and cellulose ethers [436] have been reported by various research groups. *Armes et al.* have recently shown that polyaniline and polypyrrole colloids can be prepared by using colloidal silica [437-441] and, incase of poylpyrrole, also tin oxide sols [442] instead of polymeric stabilizer. The electrical conductivity measurements of polyaniline-silica composite [442] prepared by dispersion polymerizing are illustrated Fig. 1.27. Its conductivity at 25 °C is 6.1×10^{-2} S cm^{-1}. As expected with semiconductors, the conductivity

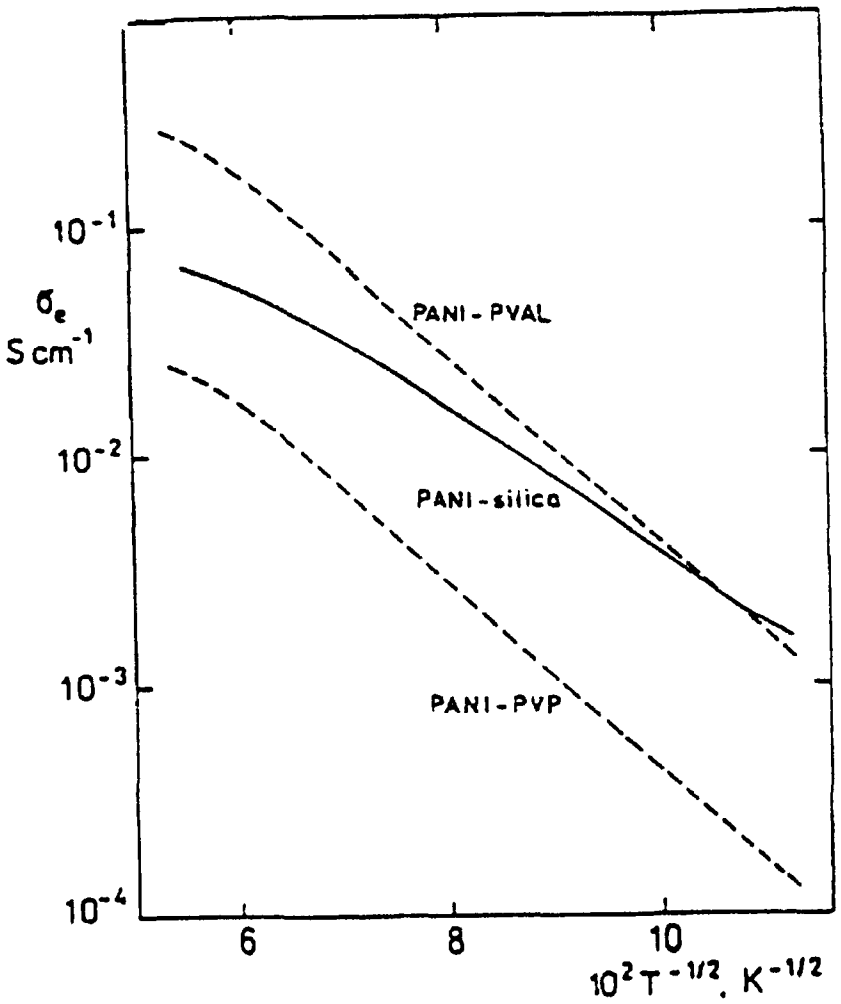


Fig.1.27. Temperature dependence of electrical conductivity, σ_c for a PANI (37.8 wt. %)-silica composite (full line) and its comparison with polyaniline (48.3 wt. %):poly(vinyl alcohol)and, polyaniline (39.4 wt. %): poly(N-vinylpyrrolidone) composites (broken lines).

increases with increasing temperature (Fig. 1.27). The electrical conductivity of the polyaniline-silica composite is virtually the same as that of polyaniline:poly(vinyl alcohol) (PVA) or polyaniline:poly(N-vinylpyrrolidone) (PVP) composites [443,444] of comparable polyaniline content (Fig.1.27). Consequently, the electrical properties are independent of the type of the stabilizer, particulate or polymeric, used for the preparation of polyaniline. Recently, several groups have also combined conductive polymers with transition metal oxides to generate hybrid organic-inorganic composites [445-448], which possess higher reversible capacity [445], redox cyclability [447] and structure stability [448]. Among the transition metal oxides, several researchers studied [449-451] the V_2O_5:PANI and V_2O_5:PPy nanocomposites. *E. Ruckenstein et al.* synthesized the V_2O_5:PANI nanocomposite, which showed a relatively high conductivity (10^{-2} Scm^{-1}) [452]. The steps of the intercalative polymerization in the mesostructured V_2O_5 are presented schematically in Fig. 1.28. Nevertheless, electronic devices based on inorganic materials still dominate the market due to their well defined and the wide spectrum of electronic properties. But the approach of organic-inorganic composites materials could quickly lead to a new generation of inexpensive computer displays or solar cells that are either flexible or embedded within curved plastic, glass or other materials. Because, wholly inorganic semiconductors require processing at high temperatures, making it impossible to embed circuits in plastic or other heat-sensitive materials. On the other hand, the new hybrid materials "self-assemble," crystallizing from a liquid solution at low temperatures to form alternating organic and inorganic layers of material with the correct semiconducting properties.

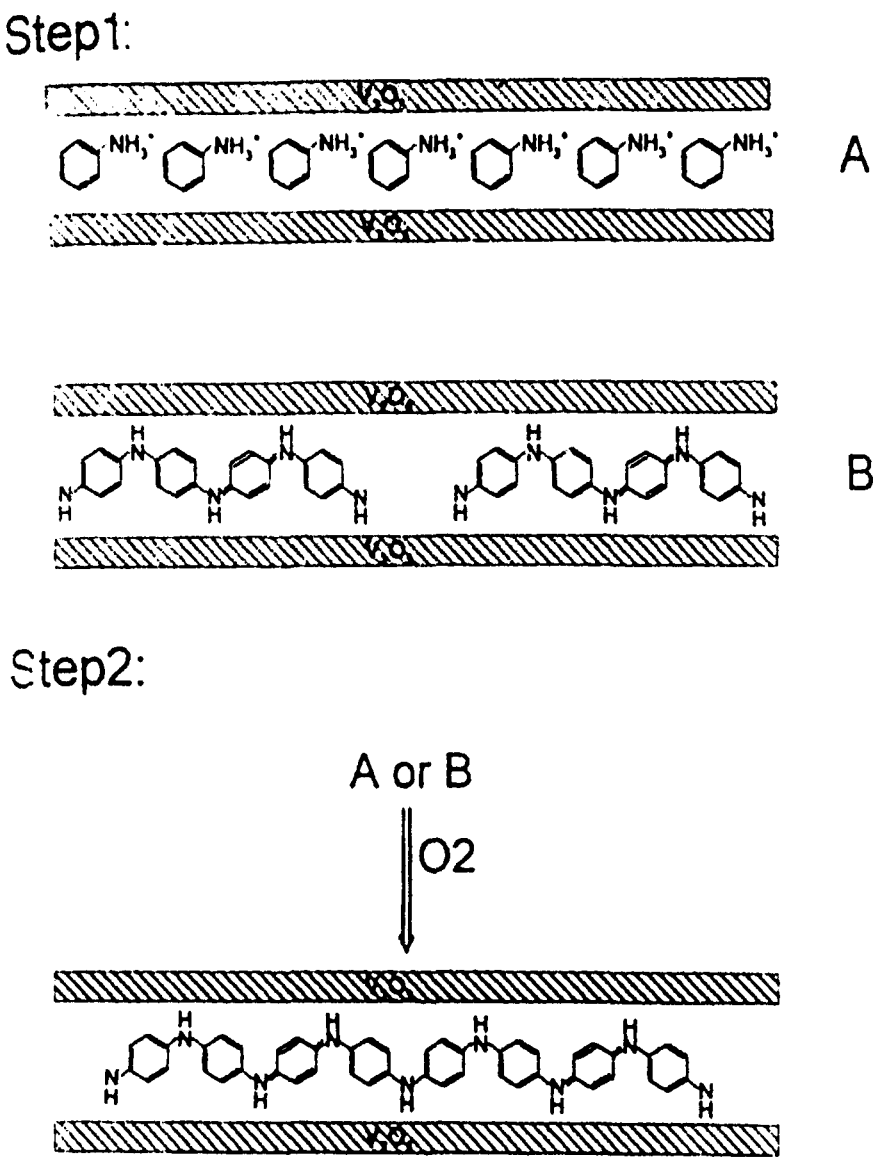


Fig. 1.28. Synthesis of a mesostructured V_2O_5:Polyaniline nanocomposite.

1.6.5. Applications of electrically conducting polymers and composites

1.6.5.1. Optical Devices

Optics was certainly one of the first applications of hybrid materials [453]. Thus, organic:inorganic/organic:organic hybrid materials with high transparency are expected to be new optical materials such as optical fiber, wave-guide and optical lens. Materials with high refractive index, low density and good transparency in visible region are in demand as optical lenses especially for glasses. In order to implement optoelectronic or photonic properties into devices, the materials have to fulfill high optical quality demands and have to be stable over a long period. Furthermore, the control of the refractive index as well as the thickness and therefore, the processibility of the materials are important. Due to its low optical losses (high optical quality), silica glass and composites made from it seem to be very useful for these devices [454,455]. For example, photoconducting composites were prepared by the incorporation of cadmium sulfide particles in a polyvinylcarbazole matrix. The resulting materials allowed the tuning of the band gap of the sensitizing nanocrystals so that their spectral response was adjusted to suit a particular wavelength of operation [456,457].

Thus, the optical properties of organic-organic/organic-inorganic composites have attracted much interest, particularly their transparency and 'active' optical properties. Transparent products can be obtained from layered systems under certain conditions. Hybrids of clay and nematic liquid crystals prepared by *Kawasumi et al.* [458], exhibit interesting electro-optical properties. These materials can be

transparent (Fig. 1.29(a)) or opaque (Fig. 1.29(c)) depending on the frequency of the applied electric field. The effect is reversible and can be repeated many times. The transparent and opaque states exhibit a memory effect after switching off the field (Fig. 1.29(b) and Fig. 1.29(d)). Such materials have potential applications in optical storage devices, displays and light-controlling glass. Another interesting example of optoelectronic 'organic-inorganic' hybrid is TiO_2/polyacrylate, which shows good visible light transparency as compared to TiO_2 as shown in Fig. 1.30. The development of optically activated hybrid organic-inorganic mesostructured silica composites has led to a number of advanced optical applications, such as optical switches and sensors and low threshold wave-guide microlasers. However, the low refractive index of silica composites (n = 1.43) requires that the optically active layer be supported by an ultra low refractive index layer for wave guiding to occur. This obstacle could be overcome by using a higher refractive index inorganic component. Recently, *D. Stucky et al.* [459] demonstrated a new synthetic approach for high refractive index, dye-activated, hybrid mesostructured materials utilizing a fluorocarbon stabilized titania precursor. These titania composites can readily be processed into solid, optically transparent, crack free fibers and planar wave-guides.

Several research groups [460-466] have studied light emitting diodes using hybrid composites. Compared to classical organic or polymer based diodes, those fabricated with composites as an emitting layers exhibited low turn-on voltage [460,461,463,464], improved stability [465]. Depending on the nature of material as well as the adopted structure, the obtained emitted light could be that of the organic

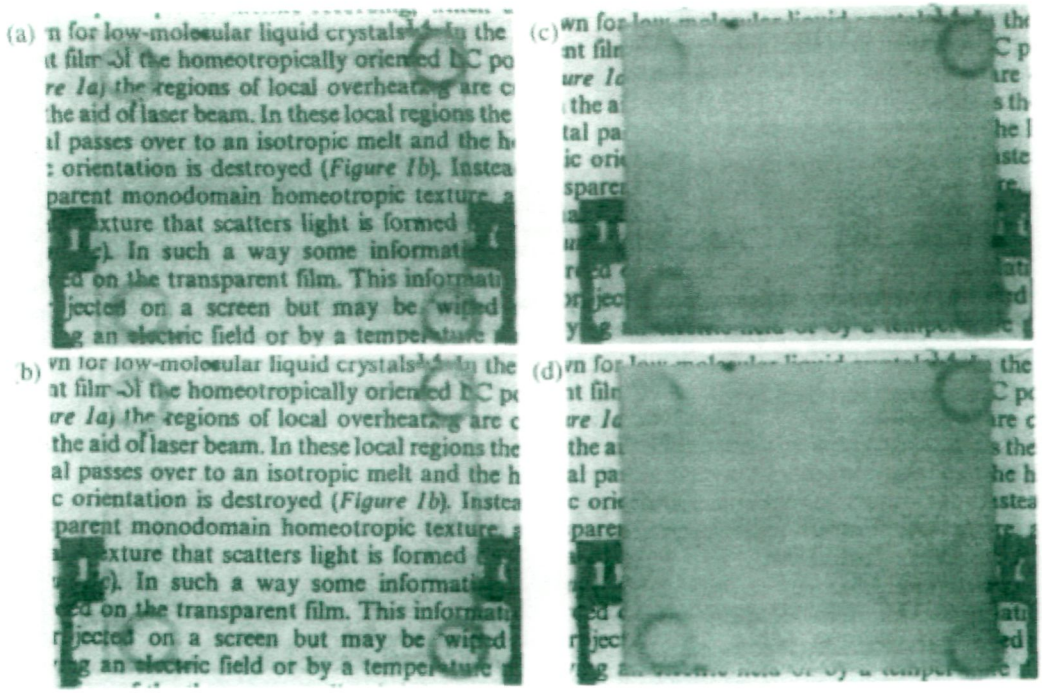


Fig.1. 29. Electro-optical properties of clay:nematic liquid crystal hybrids. (a) low frequency, on, (b) low frequency, off, (c) high frequency, on and (d) high frequency, off .

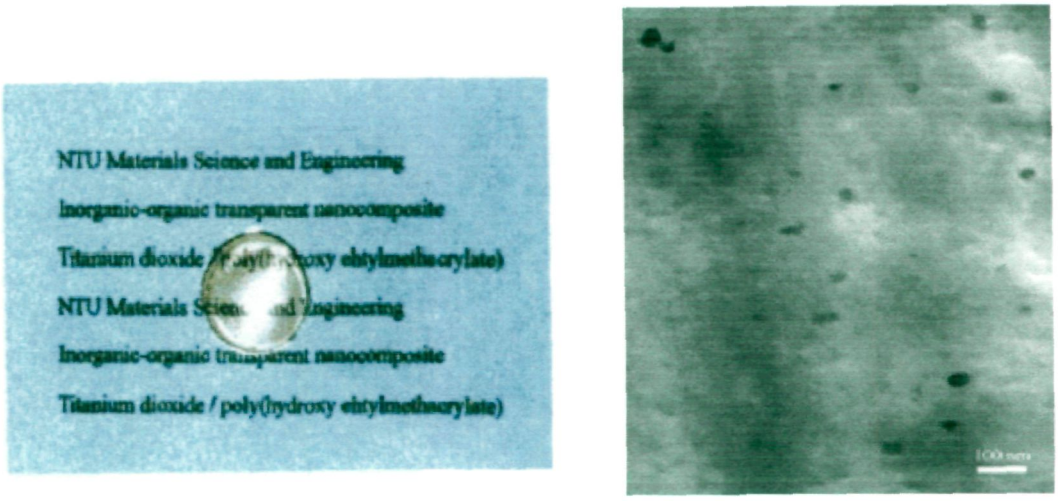


Fig.1.30. TiO_2:Polyacrylate shows good visible light transparency (left) and TiO_2 film of thickness about 20 nm (right).

[465,467] or the inorganic [462,463] or both of them as a function of the applied voltage [459,460]. Color conversion of light from short wavelength to longer one could also be achieved using particular arrangement of the layers [467].

Among conjugated polymers poly(p-phenylene vinylene)s have been studied extensively for their electro luminescence and potential applications in light emitting diodes (LEDs) because of its easy processibility and relatively good optical and electrical performance. On the other hand, porous silicon was found to have high conductivity and to exhibit interesting electroluminescence properties. Optical study of composites made of porous silicon and a non-conjugated polymer has been performed by *Guha et al.* [464,468] using mixed structures but no LEDs result was reported. The synthesis of intercalated hybrids of smectic clay and a substituted poly(p-phenylene vinylene) has also been reported. These hybrids exhibit electroluminescence and the luminescence appears to be color tunable depending on the degree of intercalation. Organically modified silicates (ormosil) and organically modified ceramics (ormocer) synthesized with sol-gel route have also been intensively studied in the last ten years due to their wide spectrum of integrated optics applications such as the fabrication of passive and active wave guides, sensors, electro-optical modulators and solid-state microlasers [469].

The desirable electrical and optical properties exhibited by the hybrid perovskites, along with the potential for simple, low-cost processing techniques, make it interesting to consider building devices with these materials. These useful optical characteristics make the perovskites attractive as potential emissive materials

in electroluminescent (EL) devices. The first attempts to induce EL in these materials involved attaching silver paint contacts to single crystals of $(C_6H_5C_2H_4NH_3)_2(CH_3NH_3)Pb_2I_7$ [470]. More recently, EL devices were prepared, with a structure analogous to that of traditional organic light emitting diodes (OLEDs), but with hybrid $(R\text{-}NH_3)_2PbI_4$, perovskite light-emitting layers [471,472]. In addition to their potential applications in 'organic-inorganic light emitting diodes (OLEDs) systems, semiconducting hybrid perovskites are also attractive as a new class of channel materials for thin-film field-effect transistors (TFTs) [473]. The 'organic:inorganic' hybrid materials are interesting for this application because they can combine the higher carrier mobilities of ionic and covalently bonded inorganic semiconductors with the simple, low-cost and low-temperature thin-film techniques that make organic semiconductors exciting as alternative channel materials. Recently, *C.R. Kagan et al.* [473] demonstrated the first 'organic:inorganic' hybrid material as the semiconducting channel in a TFT, using the hybrid perovskite $(C_6H_5C_2H_4NH_3)_2SnI_4$ Fig. 1.31 depicts a typical 'organic-inorganic' TFT device structure.

1.6.5.2. Conductors

Electrically conducting composite materials show various applications in electronic and photonic systems. Most of them show the electrical conduction behavior in the semiconductor region and hence they can be used as semiconducting materials. Nowadays, these materials have been used in the preparation of potentiometric sensors, i.e., gas sensors, chemical sensors, biosensors, ion-sensors as

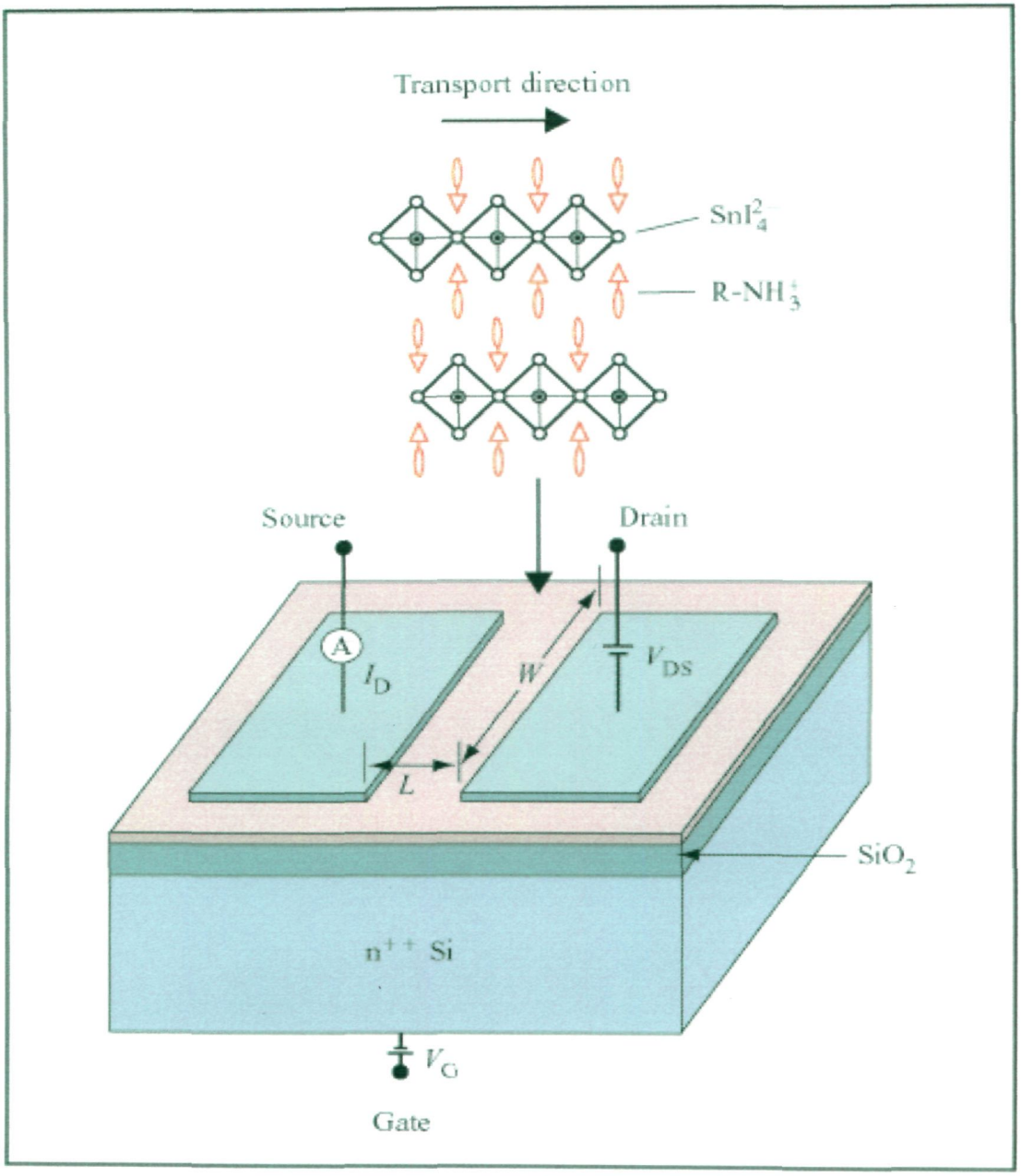


Fig. 1.31. Schematic diagram of a TFT device structure employing a layer 'organic:inorganic' perovskite.

well as ion-selective electrodes, which are of vital analytical and environmental interest. The integration of chemically sensitive membranes with solid state electronics has led to the evolution of miniaturized, mass produced potentiometric probes known as ion-selective field effect transistors (ISFETs). Thus, the electrical and electronic properties exhibited by solid-state materials are crucial in a large number of inorganic as well as organo-inorganic materials applications [474-478]. These unique electronic properties result from their extended structures, where strong interactions between the atoms, ions or molecules occur throughout the lattice. In terms of conductivity, the behavior ranges from insulating through semiconducting to metallic and superconducting many types of electrically conducting composite materials classified as electrolytes or polymer ionics have been developed and characterized in recent years [479] for applications such as solid-state lithium batteries or supercapacitors produced using 'organic:inorganic' polymeric systems formed by the mixture of organic polymers and inorganic moieties prepared by the sol–gel techniques. In these systems at least one of the network forming species should contain components that allow an interaction to the conducting ions. This is often realized using organic polymers, which allow an interaction with the ions such as poly(ethylene oxide) (PEO) [480-482]. Solid electrolytes, having conductivities of 10^{-2} to 10^{-1} Scm^{-1}, are required in several systems operating either with high current densities (electrolyzers, batteries, etc.) [483], or at very low current levels (gauges, electrochemical memories, coulometers, etc.) [484], in order to avoid excessive Joule-heat losses or excessive cell impedance. Furthermore, high conductivities are

required for materials employed in the preparation of charged membranes or in thermoelectric generators [485]. Only a few solid electrolytes are presently known to exhibit such a favorable conductance and most of them only at high temperature. The combination of conducting polymers with inorganic species is another example for nanocomposites with a potentially important application. A variety of combinations have already been tested and especially polyaniline and polypyrrole show an interesting potential in combination with iron oxides, barium titanate, platinum and tungsten oxide for magnetical, energy storage, catalytic and electrochromic devices, respectively [486]. Metallo and metal free phthallocyanines and their polymers are also known for almost a centaury and have become one of the most intensively studied macrocycles due to their resemblance to biologically occurring porphyrins [487]. They possess useful optical, electronic, electrical, photoelectric and electrochemical properties and hence, have become ideal candidates for use in the fabrication of novel electronic devices [488-499], molecular electronic devices [500-504], gas sensors and detectors [505-508]. They can be reversibly doped to achieve metallic conductivity by exposure or co-crystallization with a variety of electron acceptors. Thus, the electrical conductivity can also be improved by effecting refinements in these polymers via thermal and reactive treatments. Proton conducting composites were also obtained by the formation of interpenetrating networks (IPNs) from silicon alkoxide end-capped PEO, phenyltriethoxysilane using monododecylphosphate or phosphotungstic acid to induce the proton conductivity [509]. High temperature protonic conducting polymers membranes provide new

technological applications in the electrochemical devices including electrochromic displays, chemical sensors, fuel cells and others. Organic/inorganic composite membranes, consisting of SiO_2:PEO hybrids, are remarkable family of isotropic, amorphous polymer material, which shows good protonic conductivities at high temperatures above 100°C. At the same time hybrid materials with ionic conductivity have also been described. These hybrids are being produced by dissolving lithium salt in a suitable phase, an organically modified silica (amines, sulphonic acid, sulfonamides [510] or silica polymer networks such as poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG) etc. [511]. Transport phenomena of cations in polymeric structures have been widely studied and demonstrate that reasonable values of Li^+ mobility are reached if the surrounding solvating media also experiences a high degree of mobility [512]. In PEG:silica structures, the dependence of ionic conductivity (σ_{Li+}) on temperature demonstrate polymer like behavior, in agreement with thermal analysis and the NMR experiments which present a value of Tg in the range – 60°C to + 20°C, depending upon the exact material composition. Ionic conduction in organic-inorganic composite based on poly(propylene glycol) has been described by *R.F. Bianchi et al.* [513]. At last we can say that more and more compounds presenting electronic properties are also under study. Redox targets have been entrapped in hybrid matrices, leading to photo- or electro active materials [514]. These properties have also been used to study the change of structure during the sol-gel transition via the determination of self-diffusion coefficients [515]. These properties are also expected for redox sensors and biosensors. Because of the

flexibility of the chemistry, the redox properties of materials can be tuned. Very promising results arise from electronic conductors such as silica-polypyrrole, silica-aniline interpenetrated networks and V_2O_5-polypyrrole layered structures. The search of anisotropic conductivity properties is clear evidence by this last example. Recently, semiconductor research has also found interesting isolating materials that can be used in organic transistors and chips [516].

1.6.5.3. Sensors

Organic or inorganic semiconductors have been reported to change their conductivities when exposed to variety of organic and inorganic vapors. Thus, these materials can be expected to behave as sensors. Composite materials of tin oxide and derivatives of polypyrrole [507] gave reversible changes in electrical resistance at room temperature when exposed to a variety of organic vapors. Composite materials containing 2.5% polymer by mass were fabricated and exposed to low concentrations of ethanol, methanol, acetone, methyl acetate and ethyl acetate vapors [517-520], the composite materials were found to give more significant and reversible decrease in electrical resistance in comparison with sensors constructed solely of tin dioxide or polypyrrole. These materials could be used in the quality control of foodstuff, especially in the early detection of soft rot in potato tubers. Some researchers incorporated preformed polypyrrole and poythiophene in to clay (montmorillonite) by the interaction of colloidal nanoparticles of the polymers with the colloidal layered host [521]. This method using a colloid-colloid reaction [522] might provide a general route to incorporation of intractable polymers within layered host structures

that can be exfoliated, such as smeccice clays [523], metal disulfides and some metal oxides. These composite materials have potential to be used as hybrid sensors.

Chemical sensing properties of the electrochemically prepared polypyrrole-poly(vinyl alcohol) (Ppy-PVA) films were studied by exposing them to NH_3 gas [524]. The results shown in Fig. 1.32 reveal that the sample has a very good sensitivity towards NH_3. A remarkable increase in resistance of the sample is observed within 5 min from purging and this change is reversible within 5% of the initial resistance. Increasing the concentration of NH_3 more obvious changes are observed but NH_3 concentration above 10% results in almost reversible change of resistance.

Lastly, the possible applications of the composite materials are diverse and the future of these materials appears bright. Therefore, in general the application of composite materials can be exemplary introduced in the following field.

- ✓ Rechargeable batteries
- ✓ Electrochromic devices
- ✓ Optoelectronics
- ✓ Photovoltaics
- ✓ Field effect transistors
- ✓ Display devices
- ✓ Printed circuit board
- ✓ Chemical indicators
- ✓ Bio-sensors
- ✓ Gas sensors
- ✓ Solar cells
- ✓ Electroplating
- ✓ Conducting textiles
- ✓ Electrochemically switchable ion-exchangers
- ✓ Transparent coatings
- ✓ Adhesives
- ✓ Radiation detectors
- ✓ Schottky diodes
- ✓ Fillers
- ✓ Solid lubricants
- ✓ Corrosion inhibitors
- ✓ Photocatalysis

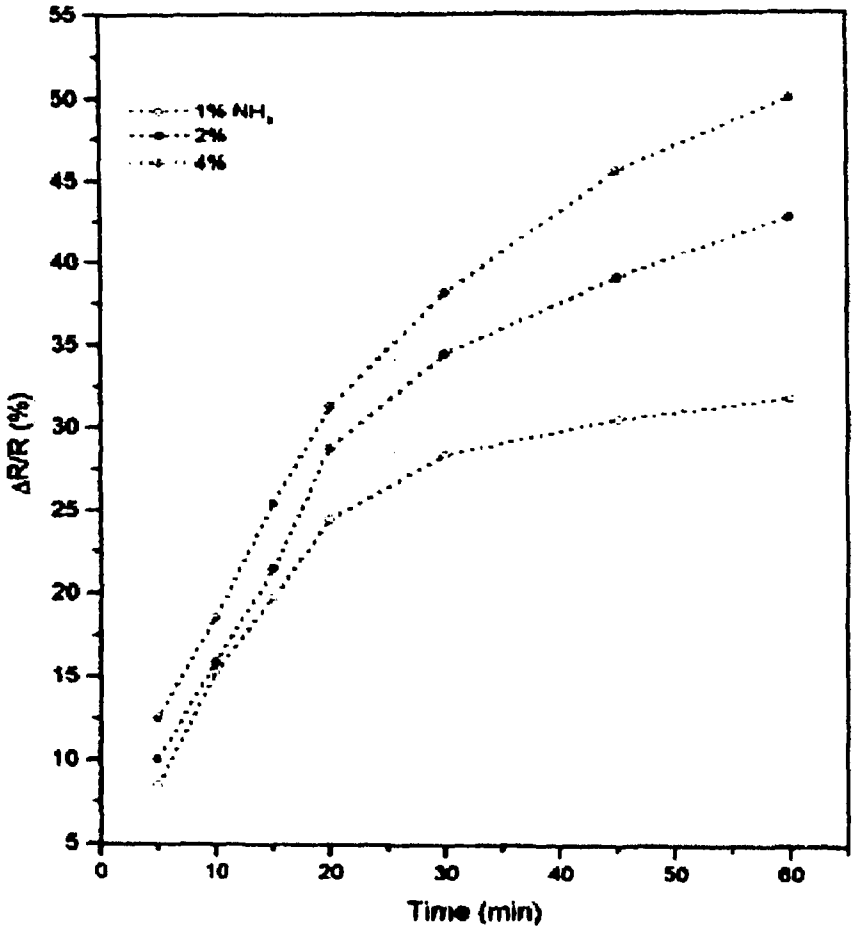


Fig.1.32. Resistance changes recorded for Ppy:poly(vinyl alcohol), interpenetrating networks on exposure to NH_3-argon mixtures of different NH_3 (%).

1.6.5.4. Electrically conducting polymers and composites as ion-exchangers

The ion-exchange behavior during charging and discharging processes of conducting polymers, *e.g.* polyaniline and polypyrrole, has been widely studied in recent years [525-536]. It was found that the conducting polymers exchange both anions and cations depending on the polymerization conditions, the type and size of the counter ions incorporated during the polymerization process as well as on the ions present in the electrolyte solution, the polymer thickness and the aging of the polymer. By an appropriate choice of counter ion conducting polymers can be tailored to work as anion or cation exchangers. Polyaniline (PANI) and polypyrrole (PPy) can work as anion-exchangers, whereas PANI and PPy modified with polyanions in the polymeric complexes such as poly(vinyl sulfonic acid) (Fig. 1.33), poly(styrene sulfonic acid), (Fig. 1.34) poly(acrylic acid), poly(methacrylic acid), poly(2-acrylamido-2-methyl-1-propenesulfonic acid), poly(methylacrylate-co-acrylic acid) [527,528,533,534] as well as inorganic polyanions, work as cation-exchangers. Such a modified polymer can be applied as electrochemically switchable ion-exchanger based on electrically conducting polymers [526,527,531,534,535] for water treatment; especially water softening. Some electrically conducting organic-inorganic composites can be used as ion-exchangers have also been reported in literature [537-544].

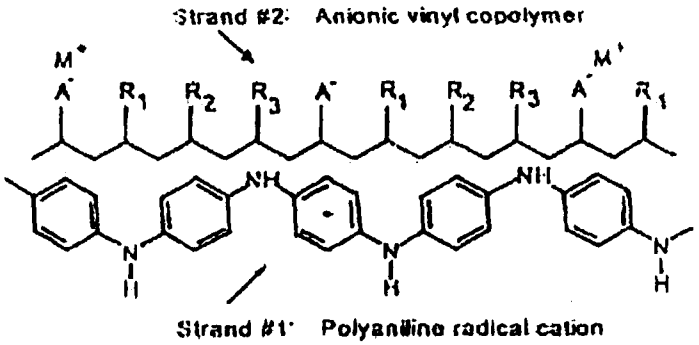


Fig. 1.33. Side-by-side molecular complex of polyaniline and a functionalized polyanion working as cation-exchanger.

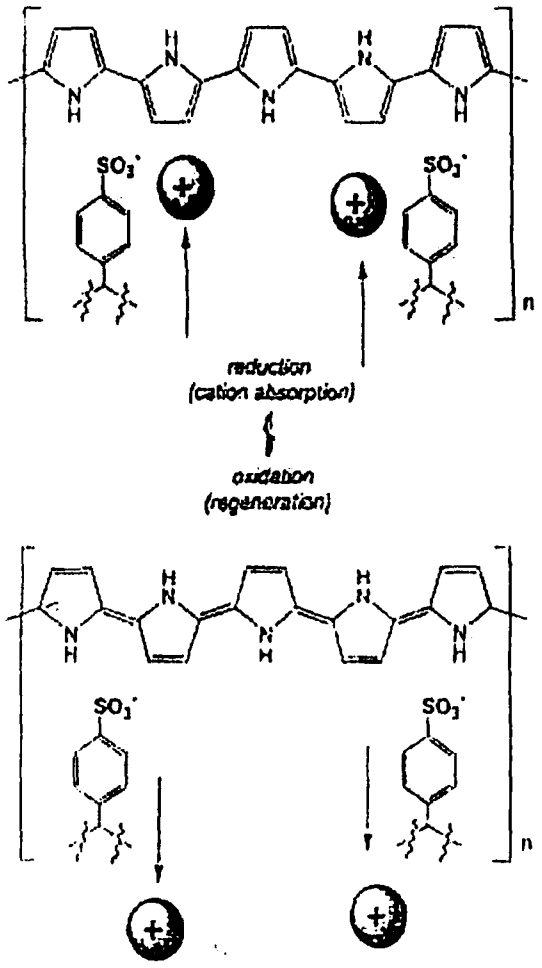


Fig. 1.34. Polypyrrole with incorporated polystyrene sulfonate counterions (PSS^-) working as cation-exchanger.

1.7. Membranes: An Introduction

A precise and complete definition of the word "*Membrane*" is difficult to make, and any complete definition given to cover all the facets of membrane behavior will be incomplete. According to *Sollner* [545], a membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the later, but permits passage, with various degree of restriction of one or several species of particles from one to the other or between the two adjacent phases or compartments, which thereby acting as a physico-chemical machine transforms with various degree of efficiency according to its nature and composition of the two adjacent phases or compartment. In simple terms, it is described as a phase, usually heterogeneous, acting as barrier to the flow of molecular and ionic species present in the liquids and for vapors containing two surfaces [546]. The term heterogeneous has been used to indicate the internal physical structure and external physico-chemical performance [545,547,548]. From this point of view, most of the membranes in general are to be considered heterogeneous, despite the fact that, conventionally, membranes prepared from coherent gels have been called homogeneous [549].

The usefulness of a membrane in a mass separation process is determined by its selectivity, by its chemical, mechanical and thermal stability and its overall mass transport rate. The chemical nature of the membrane material is of prime importance when components with more or less identical molecular dimensions and similar chemical or electrical properties have to be separated. The chemical, mechanical and thermal stability of the membrane determines to a large extent its useful lifetime,

especially when the feed solution contains strong solvents, strong oxidants and extremely low or high pH values, when the process has to be carried out at elevated temperatures or when frequent cleaning procedures of the membrane are required. The mechanical properties of a membrane are of special significance in pressure driven process such as reverse osmosis, ultra filtration, *etc.* Ideally, a membrane should not change its useful properties when it is derived out or when the composition of feed solution is changed drastically. For economic reasons, finally the flow rate of the permeable components through a given membrane area under a given driving force should be as high as possible to minimize investment costs which are generally proportional to the membrane area installed to give a certain process capacity. To significantly expand the use of membranes in mass separation processes beyond their present applications, membranes with more specific transport properties, longer lifetimes and higher flux rates are required.

1.8. Electrochemical Sensors

Electrochemical sensors represent an important subclass of chemical sensors in which an electrode is used as the transduction element. According to such devices hold a leading position among sensors presently available, having reached the commercial stage, and have found a vast range of important applications in the field of clinical, industrial, environmental and agricultural analyses. The field of sensor is interdisciplinary, and future advances are likely to occur from progress in several disciplines.

Potentiometric sensors work through the measurement of an equilibrium potential *i.e.*, the potential at zero current, of the sensor versus a suitable reference electrode. These potentials are a function of the activity of the species in solution, not of their concentration. The *Debye-Huckel equation* relates concentrations to activities and can often be employed; indeed potentiometric measurements can be used to test the *Debye-Huckel theory*. However, for dilute solutions it is reasonable to assume that activity and concentration are equal. There are few reviews [550,551], which compare potentiometric and amperometric sensors in terms of their performance and limitations. However, the rapid development of new selective electrodes and more sensitive and stable electronic components over the past 25 years has expanded tremendously the range of analytical applications of potentiometric measurements. The speed at which this field has developed is a measure of the degree to which potentiometric measurements meet the need of the analytical chemist for rapid low-cost and accurate analysis. Many general books have been devoted exclusively to direct potentiometry [552-554]. Several review articles have been appeared in literature time to time [555-561].

1.8.1. Ion-selective electrodes

Ion-selective electrodes are mainly membrane-based devices; consist of perm-selective ion-conducting materials, which separate the sample from the inside of the electrode. On the inside is a filling solution containing the ion of interest at a constant activity. The membrane is usually non-porous, water insoluble and mechanically stable. The composition of the membrane is designed to yield a potential that is

primarily due to the ion of interest (via selective binding processes, *e.g.* ion-exchange, which occur at the membrane-solution interface). The purpose is to find membranes that will selectively bind the analyte ions, leaving co-ions behind. Membrane materials, possessing different ion-recognition properties, have thus been developed to impart high selectivity.

The Ion-Selective Electrodes (ISEs) are commonly known as "Ion Sensors" or "Electrochemical Sensors". The history of ion-selective electrodes in the past decade shows the typical behavior of expansion followed by consolidation. The rapid growth of new electrodes for ion activity measurement, new formats and new material of construction has given a way to more in prospective research on "How and Whys" of the functioning of various electrodes and extensive application studies, uses of ISEs as instrumental components and in diverse field, particularly in clinical and environmental chemistry.

1.8.2. Physico-chemical properties of ion-selective electrodes

In order to study the characteristics of the electrode, the following parameters were evaluated: electrode response or membrane potential, lower detection limit, slope response curve, response time, working pH range, *etc.*

1.8.2.1. Electrode response or membrane potential

The use of ion-selective electrodes depends on the determination of potentials [562,563]. The potentials cannot be determined directly but can be easily derived from the e.m.f. values for the complete electrochemical cells which comprise the membrane separating solutions 1 and 2 as well as the two reference electrodes when the ion

exchange membrane separates two solution 1 and 2 both containing the same counter ion or A, a membrane potential (E_m) is developed across the membrane due to the diffusion of counter ions from the higher to the lower concentration. The membrane potential is expressed in equation (1.6):

$$E_m = \frac{RT}{Z_A F}\left[\ln\frac{[a_A]_2}{[a_A]_1} - (Z_y - Z_A)\int_1^2 t_y d\ln a\pm\right] \quad \ldots\ldots 1.6$$

where A = counter ion, Y = co-ion, Z = charge on ions, t_Y = transference number of co-ions in the membrane phase, $[a_A]_1$ and $[a_A]_2$ = activities of the counter ions in the solution 1 and 2, $a_\pm$ = mean ionic activity of the electrolyte. It is quite evident from the equation that 'E_m' is the sum of diffusion and *Donnan Potential*. In equation (1.6) the right hand side consists of two terms, the first term represents the thermodynamic limiting value and the second term denotes the diffusion potential due to co-ion flux membrane.

If the membrane is considered to be ideally perm-selective membrane ($t_y - 0$) then equation (1.6) takes the form of the well known *Nernst Equation* as follows:

$$E_m = \pm\frac{RT}{Z_A F}\ln\frac{[a_A]_2}{[a_A]_1} \quad \ldots\ldots 1.7$$

The equation (1.7) simply represents *Donnan potential* for an ideally perm-selective membrane or it can be said that it gives the thermodynamic limiting value of concentration potential. Equation (1.7) takes positive sign for cations and negative sign for anions. The membrane potential measurement is carried out using a cell set up of the following type:

Solution 2			Solution 1	
External Saturated Calomel Electrode (SCE)	Test or External Solution	Membrane	Internal Solution	Internal Saturated Calomel Electrode (SCE)
	$E_L(2)$		$E_L(1)$	

In general practice, the concentration of one of the solution (say 1) is kept constant (usually 0.1 M) and this solution is referred as internal or reference solution and a SCE is dipped in this internal solution as an internal reference electrode. The membrane together with internal solution and internal reference electrode is one compact unit, which as whole is called as membrane electrode. This membrane electrode is then immersed in solution 2, usually referred as external solution or test solution, having an external reference electrode. The e.m.f. of this potentiometric cell is given by the following expression:

$$E_{cell} = E_{SCE} + E_{L(2)} + E_m + E_{L(1)} - E_{SCE} \quad \ldots\ldots 1.8$$

where E_{SCE}, E_L and E_m refer to Calomel Electrode, junction and membrane potentials, respectively. On combining equation (1.7) and (1.8), the following equation takes the form-

$$E_{cell} = E_{SCE} - E_{SCE} + E_{L(2)} + E_{L(1)} \pm \frac{RT}{Z_A F} \ln \frac{[a_A]_2}{[a_A]_1} \quad \ldots\ldots 1.9$$

For cation-exchange membrane,

$$E_{cell} = E_{L(2)} + E_{L(1)} - \frac{RT}{Z_A F} \ln [a_A]_1 + \frac{RT}{Z_A F} \ln [a_A]_2 \quad \ldots\ldots 1.10$$

As the activity of internal solution is kept constant and the values of $E_{L(1)}$ and

$E_{L(2)}$ are also almost constant, the term in parenthesis may be taken equal to a constant, E^o. Furthermore, the values of $E_{L(1)}$ and $E_{L(2)}$ are negligible (due to salt bridge in use), the cell potential in above equation may approximately be taken as membrane potential. The equation (1.10) reduces to-

$$E_{cell} = E^o + \frac{RT}{Z_A F} \ln [a_A]_2 \qquad \ldots\ldots 1.11$$

Now, it is quite clear from equation (1.11) that the cell potential would change with the change in concentration (or activity) of the cation in external or test solution 2. At 25 °C, value of RT/Z_AF comes out to be $0.059/Z_A$ volts. The membrane is said to give Nernstain response if the slope of a plot between cell potential and log activity comes out to be $0.059/Z_A$ volts. These plots are called Nernst plots and the slope as Nernstian slope.

From the calibration graph, it can be observed that the response curve is linear down to a particular concentration after which the curve tends to become parallel to the x-axis. Suitable concentrations were chosen corresponding to the sloping portion of the linear curve for the measurement of potentials. The slope of this linear curve is important and tells whether the electrode response follows the Nernstian response or not. A potentiometric sensor is said to be behaving in a Nernstian or close to Nernstian fashion, if the slope is ±1-2 mV of the theoretical value. Below this range it is sub-Nernstian, above it, it is hyper-Nernstian. Sensors which are outside the Nernstian range can still be useful analytically.

1.8.2.2. Selectivity coefficients

A selectivity coefficient is one of the most important factors of ion-selective electrodes (ISEs), on the basis of which the potential application of an electrode in a given system can be predicted. Generally, ISEs are mainly membrane-based devices, consisting of perm-selective ion-conductive materials, which separate the sample from the inside of the electrode. Inside the electrode, a filling solution containing the ion of interest at a constant activity is taken into consideration. The membrane is usually non-porous, water-insoluble and mechanically stable. The composition of the membrane is designed to yield a potential that is primarily due to the ion of interest. The purpose is to find membranes that will selectively bind the analyte ions, leaving co-ions behind. Thus, membrane materials, possessing different ion-recognition properties, have been developed to impart high selectivity. Detailed theory of the processes at the interference of these membranes, which generate the potential, is available elsewhere [564-566]. Such a potential arises whenever the membrane separates two solutions of different ion activities. The resulting potential of the ion-selective electrode, which reflects the unequal distribution of the analyte ions across the boundary, is generally monitored relative to the potential of the reference electrode. Since the potential of the reference electrode is fixed, the measured cell potential reflects the potential of the ISE, and can thus be related to the activity of the target ion. Ideally, the response of the ISE should obey equation (1.12):

$$E = E^{o} + (2.303\ RT/Z_i f) \log a_i \qquad \ldots\ldots 1.12$$

However, equation (1.12), has been written on the assumption that the electrode

responds only to the ion of interest, '*i*'. In practice, no electrode responds exclusively to the ion specified. The actual response of the electrode in a binary mixture of the primary and interfering ions ('*i*' and '*j*', respectively) is given by the *Nikoloskii-Eisenman* equation [567]:

$$E = E^{o} + (2.303\ RT/Z_i f) \log(a_i + K_{ij}^{pot}\ a_j^{\ Z_i/Z_j}) \quad \ldots\ldots 1.13$$

where E = potential of the electrode, E^{o} = standard potential of the electrode, a_i = activity of '*i*' ions, a_j = activity of '*j*' ions, Z_i = charge on the '*i*' ion, Z_j = Charge on the '*j*' ion, K_{ij}^{pot} = selectivity coefficient of the electrode in the presence of *j* ions, which measure the relative affinity of ions '*i*' and '*j*' towards the ion-selective membranes.

No electrode is absolutely selective for a particular ion. Thus, the selectivity of the electrode depends on selectivity coefficients. The lower the value of K_{ij}^{pot}, the more selective is the electrode. For ideally selective electrodes, the K_{ij}^{pot} would be zero. So, it is important for the analytical chemist to realize the importance of selectivity coefficient of a particular electrode. The inconsistent values of selectivity coefficient may cause problems [568-570]. Various methods [571] have been suggested for determining the selectivity coefficient, however, it falls in two main groups, namely- (1) Separate-solution method and (2) Mixed-solution method.

Separate-solution methods [572-574]: In the separate-solution method, the potential of the electrode E_i and E_j are measured separately in solutions containing '*i*' only of activity a_i (no '*j*' present) and '*j*' only of activity a_j (no '*i*' present), respectively and are given by the following equations:

$$E_i = E^{o} + (2.303\ RT/Z_i f) \log a_i \quad \ldots\ldots 1.14$$

$$E_j = E^{o} + (2.303\ RT/Z_j f) \log K_{ij}^{pot}\ a_j \quad \ldots\ldots 1.15$$

K_{ij}^{pot} can be calculated either with the so-called equal activity or with the equal potential method. In both cases, it is assumed that the electrode standard potentials are equal in the presence of ion '*i*' as well in that of ion '*j*' and also that the response is Nernstain for both ions. According to the method of equal activities the solution of ion '*i*' and '*j*' are prepared at the same concentration and the potentiometric measurements are carried out. From the equations (1.14) and (1.15), we get

$$\log K_{ij}^{pot} = \frac{E_j - E_i}{2.303RT/Z_iF} + \log \frac{a_i}{(a_j)^{Zi/Zj}} \quad \ldots\ldots 1.16$$

The term $2.303RT/Z_iF$ is the slope of Nernst plot. As most of the solid membranes exhibit deviation from Nernstian behaviour, the experimental slope (S), usually differs from the theoretical slope *i.e.*, $2.303RT/Z_iF$. Thus, it is a practice to use 'S' instead of Nernstian slope for the calculation of K_{ij}^{pot}. As such equation (1.16) takes the form.

$$\log K_{ij}^{pot} = \frac{E_j - E_i}{S} + \log \frac{a_i}{(a_j)^{Zi/Zj}} \quad \ldots\ldots 1.17$$

Thus, using equation (1.17) selectivity coefficient K_{ij}^{pot} can be calculated. The separate solution technique for determining selectivity coefficients is simple and allows a number of K_{ij}^{pot} values to be measured on the basis of different activities and potentials.

Mixed solution methods [575-581]: In the mixed solution techniques, the electrode potentials are measured in solutions containing both the primary ion '*i*' and the interfering ion '*j*'. There are two procedures for determining the selectivity coefficients using Mixed Solution Method.

Procedure 1 In this procedure, the potentials of the electrode E_i and E_{ij} are measured in solutions of primary ion '*i*' only and a mixture of primary and interfering ion '*j*', respectively.

$$K_{ij}^{pot} = \log [10^{(E_{i+j} - E_{i/m})} - 1] + \log a_i - Z_i/Z_j \log a_j \quad \ldots\ldots 1.18$$

Or, in other form, it can be writen as

$$K_{ij}^{pot} = \frac{a_i}{a_j^{(Zi/Zj)}} \left(\left\{ 10^{\frac{E_{i+j} - E_i}{2.203\, RT/ZiF}} \right\} - 1 \right) \quad \ldots\ldots 1.19$$

Procedure 2 In this method, the selectivity coefficients were calculated by the following procedure:

When electrode potentials measured in a number of solutions of varying a_i and constant a_j are plotted against the activity a_i, a curve of the type shown in Fig. 1.35 is obtained. This plot generally has three distinct regions. In the first region PQ, the response of the electrode is linear that indicates the electrode is responding only to primary ion '*i*' with no interference caused by '*j*' in this concentration range. In the second region QR, derivation from linearity is caused because now the electrode also responds to the activity of '*j*' as the concentration of '*i*' decreases. So, in this region (QR), the response of the electrode is mixed and is due to both the ions '*i*' and '*j*'. The third region (RS) indicates that the electrode is now only responding to interfering ion '*j*' with no contribution arising due to primary ion '*i*'. This generally occurs at lower activity of '*i*'. As the activity of '*j*' is constant and '*i*' is not affecting the potential in this concentration range, the potential of the electrode remains constant. The linear portion PQ and RS are then extrapolated to point T. The potential corresponding to

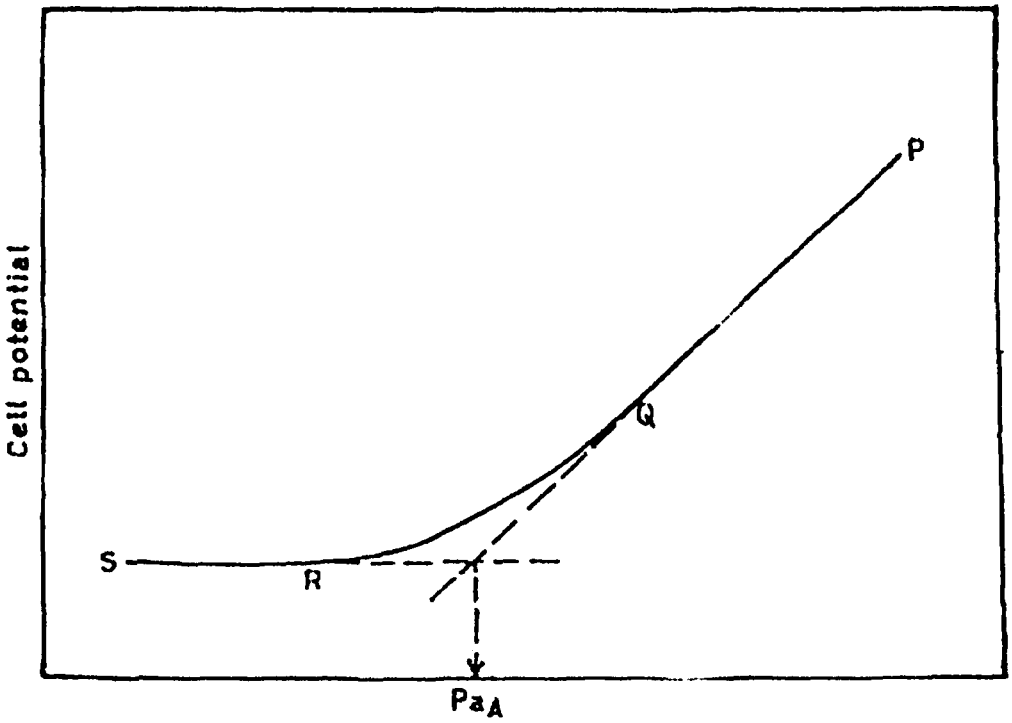


Fig. 1.35. Calibration curve illustrating determination of selectivity coefficient by fixed interference method (FIM).

point T can be generated by constant activity of '*j*' or by the activity of '*i*' corresonding to point T. Thus for point T, E_i is equal to E_j (E_i is generated by '*i*' of activity a_i and E_j by '*j*' of activity a_j). Under this condition of $E_i = E_j$, the following equation is obtained from equatin (1.19) –

$$K_{ij}^{pot} = \frac{a_i}{a_j^{(Zi/Zj)}} \qquad \ldots\ldots 1.20$$

The value of $K_{ij}^{pot} = 1$ at $Zi = Zj$ indicates equal response to both '*i*' and '*j*'. Similarly the values of $K_{ij}^{pot} < 1$ indicates that the sensor responds more to '*i*' in comparison to '*j*' and *vice-versa* for $K_{ij}^{pot} > 1$. However, when $Zi \neq Zj$, the value of selectivity coefficients indicating equal response to primary (*i*) and interfering (*j*) ions.

This method is also known as Fixed Interference method (FIM) and is the most widely used procedure as per IUPAC recommendation for determining selectively coefficients. In conclusion, it must be pointed out that the selectivity coefficient data depends to a great extent on the method used for the determination and also on the concentration level of the primary as well as the interfering ion, and on the nature of the electrode membrane.

1.8.2.3. Response time

Another important factor besides linear response that commends the use of ISEs or membrane electrode is the promptness of the response of the electrode. The response time of an ion-selective electrode is the time needed to attain equilibrium value (*i.e.* to obtain a steady potential) within ±1 mV after a ten-fold increase or decrease in the concentration of the test-solution. However, the interpretation of response time varies from a group of workers to others. *Punger et al.* [582-585] have discussed this aspect in details.

1.8.2.4. Effect of pH

The membrane electrodes with polymer binders like PVC do response to change in the pH value of the solutions. So it is necessary to study the effect of pH and the favorable working range of pH has to be evaluated for accurate measurements. Since in membrane electrodes one or other polymeric binder was used for the construction of the membrane, it is necessary that one finds out the effect of pH on the electrode response. The electrode could be safely used for measurements of their ions provided the pH of

the solutions used falls in the range where the electrode response does not change with the pH, and this pH range is used as working pH range of the electrode.

1.8.2.5. Life span of membrane electrode

Ion-exchanger membrane electrodes can be used for one to three months in continuous service. This short lifetime may be related to the gradual loss of the ion-exchanger through the porous membrane. The membrane, internal filling solution and the ion-exchanger are replaced when the electrode response becomes noisy or drifts.

So, in order to find out the life time of the electrode, the electrode response were noted every week and response curve is drawn for the data usually at the initial period some changes in the response are noted *vis-à-vis* the slope of the response curve but after the week or so, the electrode response remains fairly constant over a period of time after this period the electrode starts behaving erratic, therefore cannot be used for any measurements. This period over which the electrode response is constant can be called a life of electrode. The life of studied membranes ranges from 45 to 120 days.

1.8.3. Literature review on membranes and ion-selective electrodes

At present the membrane technology has been a thrust area of research. The membrane research involves several scientific disciplines. Polymer chemists, physical chemists, chemical engineers, medical professionals, bio-technologists and environmentalists, all are keenly taking interest in the membrane science and technology. A number of separation processes like electrodialysis, ultrafiltration, hyper filtration (reverse osmosis), microfiltration, nanofiltration and gas separation

processes involve the membranes in one way or the other way. A particular category of membranes has also been used as potentiometric sensors. The present thesis deals with the ion-exchange membranes obtained by embedding composite ion-exchangers as electroactive materials in polymer binders, *i.e.* epoxy resin (Araldite) or poly(vinyl chloride) (PVC) and have been extensively studied as potentiometric sensors, *i.e.* ion-sensors, chemical sensors or more commonly ion-selective electrodes. Keeping these limitations in mind the review is confined mostly on the ion-exchange membranes mainly studied as potentiometric sensors.

A large number of ion-selective electrodes using ion-exchangers have been developed during the past 25 years. The literature survey reflects good volume on this topic and it is very difficult as well as unmanageable to compile all of them here. The research work on these ion-selective electrodes has begun in 1920's but their systematic studies started after *E. Pungor et al.* [586,587] in 1961. They studied the behavior of silver iodide precipitates as a model substance. Undoubtedly, the findings of *Pungor's* group given like an opening for the research in this field. These ion-selective electrodes (ISEs) become alternate of complicated instruments like visible spectrophotometer, atomic absorption spectrophotometer, inductively coupled plasma instrument and electron spectrophotometer for chemical analysis *etc.* for the determination of various cations and anions. Research in the field of ISEs was enormously stimulated by the publication by *Frant* and *Ross* [588,589] of their articles on the fluoride and calcium ion-selective electrode. A number of review articles [590-599] have come across from time to time towards the work done by various eminent persons. These review articles deals with the subject on theoretical

as well as on practical fronts. A lot of applications have also been their interest in analytical, chemical, pharmaceutical and in environmental disciplines. Most of the membranes have been prepared in the form of pellets by pressing the material in an inert polymer like PVC, silicone rubber, polystyrene, polyethylene *etc.* Use of PVC matrix membrane is not by any means restricted to ion-selective electrodes and the simple fabrication can easily put their selectivity to wider service in selective extraction and even for the transport of ions against their concentration gradients.

An epoxy resin (*e.g.* Araldite) first used by *Coetzee et al.* proved to be the most suitable and widely used material. They have worked on thallium(I) heteropolyacid salt-epoxy resin membranes in their studies and they also have determined Cs^+ potentiometrically [600,601]. Tungstoarsenate based ion-selective membranes have been developed by *Malik et al.* [602] and found very much suitable in the determination of Cs^+ and Tl^+ ions. However, there have been only a few reports concerning thallium(I) ion-selective membrane electrodes [603-612]. They need to be improved with regard to their low selectivities against alkali metal ions, linearity and pH-dependence [612]. The thallium(I) selective electrodes based on crown ether were described [607-610]. These crown ether-based ISEs exhibited good slope of calibration plots and the electrode response was stable over a wide pH range. However, the Tl^+ selectivity against K^+ for one of the bis(15-crown-5)s was fairly poor [607]. *Yamashoji et al.* [613] found that Tl^+-selective PVC membrane electrodes based on dibenzo-20-crown-6 (DB20C6) and dibenzo-22-crown-6 (DB22C6) show higher selectivities to Tl^+ than that of symmetrical dibenzo-18-crown-6 (DB18C6). The electrode based on DB18C6, DB20C6 or DB22C6 showed a linear response to

the Tl^+ activity over a range of 3.2×10^{-5}-1.0×10^{-1} M $TlNO_3$ with a slope of 59 mV per decade. Calix[4] pyrrole and quinoline-carbonitriles have been reported as Tl^+ PVC based ion-selective electrodes [614,615]. *Park et al.* [616] have reported different calix[4] for the preparation of Tl^+ ion selective membrane electrodes. Recently, thallium(I)-selective membrane potentiometric sensor based on dibenzyldiaza-18-Crown-6 was reported by *Khayatian et al.* [617].

There has been widespread interest in developing ion-selective electrodes (ISEs) for determining alkaline earth metals, as they exist in diverse samples. Amongst the alkaline earth metals, most investigated and developed ISEs are Ca^{2+}-selective electrodes. The first Ca^{2+}-selective electrode was a liquid membrane electrode developed by *Ross* [589]. It was prepared by using a liquid membrane of didecyl-phosphate in di-n-octyl phosphonate. The useful Ca^{2+}-selective electrodes were developed by *Thomas, Moody* and *coworkers* [618,619] by incorporating Ca-bis[2,6-dinitro-4-(1,1,3,3-tetramethylbutyl)] phenoxide and Ca-bis[di{4-(1,1,3,3-tetramethylbutyl) phenyl}] phosphate in PVC. These electrodes have fast response time, showed good selectivity for Ca^{2+} over a large number of cations. *McKcervey* and *coworkers* [620] have reported the Ca^{2+}-selective electrodes based on Calix[6] arene tetraphosphine oxide with excellent characteristics. The ligand, calix[6]arene bearing phosphine oxide ligand groups on the lower rim and this is the first report that such ligands can discriminate in favor of calcium ions against magnesium ions and other alkaline metal ions. This calcium selectivity is in complete contrast to the behavior of the known calix[6] arene tetraester derivatives, which are selective for sodium against other alkali metal ions and group II ions. Electrodes based on PVC

membrane incorporating ligand display almost Nernstian slopes and excellent selectivity against common interferents, including magnesium. The electrodes demonstrated effective lifetimes of at least 7 weeks and very fast response times.

Didina et al. [621] studied the influence of H^+, Li^+ and Cs^+ on the potential of the Ca^{2+}-selective PVC electrode membrane comprising thenoyl trifluroacetone, a complexing ion-exchanger and triheptylphosphate, as a plasticizer. The anomalous behavior of these cations was explained by the formation of association between cations and ion-exchanger. *Chattopadhyaya* and *Misra* [622] reported the Ca^{2+}-selective heterogeneous precipitate based membrane using Ca(II) rhodizonate as the electroactive material. The electrode was used as an indicator electrode in the precipitation titration of $CaCl_2$ with $Na_2C_2O_4$.

Little work has been done on the developments of ISEs for two alkaline earth metal ions, Mg^{2+} and Sr^{2+}. Only few such electrodes are reported which show interference to other alkaline earth metal ions. Recently, an electrode prepared using a membrane of phenylene bis(ditolylphosphinoxide) in PVC was reported as Mg^{2+}-sensor [623]. The electrode showed good selectivity towards Mg^{2+} over Ca^{2+} and worked well in the concentration range 6.0×10^{-5}- 1.0×10^{-1} M. Another electrode for Mg^{2+} has been developed by *O'Donnell* and *coworkers* [624] using various octamethylene bis(malonic acid diamides) and tris(malonic acid diamides) in PVC with 2-nitrophenyloctyl ether as solvent mediator. *Maj-Zurawska* [625] has reviewed the requirements for the magnesium ionophores used in ion-selective electrodes. The search for the best magnesium ionophores, in particular having good selectivity for magnesium over calcium led to study of different groups of compounds, β-dikctones,

monoamides of carboxylic acids, bis- and tris-malondiamides, as well as some of their compounds. As the analytical applications of magnesium ion-selective electrodes are mainly connected with clinical analysis, so the possibility of simple determination of ionized magnesium in blood offers a number of diagnostically important information in medicine.

The characteristics of Mg^{2+}-selective electrode with a polymeric membrane and self-made electrode body are presented by *Leoca* and *coworkers* [626]. Membranes are based on PVC-HMW, with different plasticizers N,N'-diheptyl-N,N'-dimethyl-1,4-butanediamide (ETH 1117) as neutral ligands and a various amounts of lipophilic salt. The electrode exhibits a linear response in the concentration range 10^{-5}-10^{-1} M Mg^{2+} ions with a slope of 23.1 mV/decade. The electrode showed good selectivity towards Na^+ and K^+ and presented considerable interference from Ca^{2+}. The pH of the test solution influences the response which was found to be over pH = 10 and under pH = 5. *Meyerhoff et al.* [627] described the effect of non-ionic surfactant containing poly(ethylene oxide) units (Brij 35 and Triton X-100) within these structure and alkyl-N-methyl glucamide (MEGA) based surfactants on the potentiometric response of neutral carrier based Mg^{2+}-selective electrodes. Results are presented for plasticized PVC membranes doped with Mg carrier ETH 7025 along with the lipophilic anionic additives. Experiments were carried out in model electrolyte solutions and the compositions were found to be similar to that of the blood serum. The ion selectivities of Mg^{2+}-selective membrane electrodes can be affected greatly by the presence of Brij 35 or Triton X-100 in the sample.

The first useful Sr^{2+}-selective electrode was developed by *Baumann* [628] using strontium complex of polyethylene glycol as electroactive material. The electrode was selective towards Sr^{2+} over Ca^{2+} and other bivalent cations with the exception of Ba^{2+} and Hg^{2+}. *Srivastava* and *Jain* [629] have reported a heterogeneous membrane using hydrous thorium oxide embedded in polystyrene while *Jain et al.* [630] have used strontium tungstoarsenate in araldite for Sr^{2+}-selective electrodes. The membrane electrode has been used as an end point indicator in the potentiometric titration involving Sr^{2+} ions against diammonium hydrogen phosphate. *Jain et al.* [631] have also reported strontium(II)-selective potentiometric sensor based on ester derivative of 4-tert-butylcalix[8] arene in PVC matrix. The sensor exhibited a good potentiometric response to Sr^{2+} over a wide range 3.2×10^{-5}-1.0×10^{-1} M with a Nernstian slope 30 mV per decade. The membrane electrode was utilized in the potentiometric titration of Sr^{2+} against EDTA. Cs^{+} ion-selective membrane electrode based on ethylene glycol-functionalized polystyrene microspheres into a palsticized PVC matrix containing sodium tetrakis-[3,5-bis(trifluromethyl)phenyl] borate as ion-exchanger was developed by *Peper et al.* [632]. The electrodes were evaluated with respect to Cs^{+} in terms of selectivity, sensitivity and dynamic response.

Ba^{2+}-selective polymeric membrane electrodes have been constructed from lipophilic electrically neutral carriers [633] and neutral carboxylic polyether antibiotic [634,635] and have been found suitable for the titration of Ba^{2+} in non-aqueous media as well as for the determination of SO_4^{2-} in the combustion products. The membranes of benzo-15-crown-5 and its Ba^{2+}-complex prepared by using an

epoxy resin binder were also found suitable as Ba^{2+}-sensor [636]. These electrodes showed good selectivity for Ba^{2+} and also used for the titration of Ba^{2+} against SO_4^{2-}. *Thomas* and *coworkers* [637] have prepared two ISEs for Ba^{2+} that make use of the membranes of non-ionic, Antarox CO-880 and it's Ba-complex in PVC matrix. The electrodes were assessed for measuring SO_4^{2-} by analate subtraction. *Bouklouze* and *coworkers* [638] have used ethylene/vinylacetate-based membranes of binaphthyl polyether as Ba^{2+} sensors. The sensors worked in the concentration range 3.0×10^{-6} - 1.0×10^{-1} M Ba^{2+} and have been used as indicator electrodes for determining the end point in the potentiometric titration of SO_4^{2-} in mineral water.

Zhang [639] published a micro review on the determination of rare earth with ion selective electrodes. The review reports the construction of rare earth electrodes, the types of electroactive materials including metal oxides, salts and rare earths containing polymers and organic reagents used. *W. Jinlan et al.* [640] prepared a heavy rare earth ion-selective electrode containing Ag/AgCl as an internal electrode using ytterbium-containing polystyrene as the active material. The electrode is found to be feasible for the determination of heavy rare earths at pH 5.5-6.3 in flow injection system. Solid-state electrodes were prepared in PVC matrix showed the better sensitivity than other electrodes for the rare earth determination [641-643]. *Chattopadhyaya et al.* [644] prepared the coated wire ion selective electrode (CWISE) for La(III) using lanthanum(III)-p-nitrobenzeneazo-chromotrope-213 as an electroactive material. *Agarwal et al.* [645] have reported the rare earth hydroxamate complexes as sensor material for the ion-selective electrodes. The use of crown ethers in the determination of rare earth metal ions has also been explored. *Shih* [646]

has reported the Cs^+ selective PVC membrane electrodes based on 15-crown-5-phosphotungstic acid (PW), 12-crown-4-PW, 1,4-dithia-12-crown-4 and 1,4-dithia-15-crown-5 as neutral carriers. These crown ether electrodes exhibited good linear response of 60 mV/decade for cesium. *Pan et al.* [647] synthesized the saturated urushiol crown ether rare-earth complexes (Ln = La-Nd) by the reaction of lanthanide nitrate and DSU 30C10 in acetonitrile solution. The lanthanum ion-selective electrode exhibited the linear responses in 1×10^{-2} - 1×10^{-6} M $La(NO_3)_3$. This electrode showed better selectivity than other La(III) electrodes reported in the literature.

Only few zinc selective electrodes [648-659] are reported in literature and most of them have poor sensitivity, selectivity, long response time and short life time [648-655]. An electrode was fabricated by incorporating zinc salts of bi(4-octylphenyl) hydrogen phosphate in PVC matrix [648] but the electrode showed serious interference from some metals. *Linnersund and Bhatti* [649] tried zinc complex of bis(2-ethylhexyl) phosphate, an extractant, as electroactive material for preparing Zn^{2+}-selective electrodes but it had a very narrow working pH of range 4.5-6.0.

Lebedeva and Jansons prepared Zn^{2+}-selective electrodes using saturated solutions of Zn-quinoline-8-carbodithioatein chloroform [650]. *Kojima and Kamata* [651] used tetrabutylthiuram disulfide as the carrier in PVC based membrane electrode. Zinc orthophosphate and zinc mercuric thiocyanate [652] were used by *Rocheleaw and Purdy* as electroactive material on a carbon support for the fabrication of Zn^{2+}-selective sensors. The electrode worked well but suffered interference from Cu^{2+}, Cd^{2+} and Pb^{2+}. Another electrode, based on salicylaldoxime-

formaldehyde resin, for zinc [653] exhibited a working concentration range of 3.0 μ M - 0.1 M with a near Nernstian slope. A zinc-selective electrode was used by *Obmetho et al.* [654] for the determination of zinc in zinc alloys. *Srivastava et al.* [655] used a cryptand for the fabrication of zinc selective sensor but it exhibited a non-Nernstian response. Zn-bis(2,4,4-trimethylpentyl) thiophosphinic acid complex was also used for fabricating Zn^{2+}-selective sensor [656] but it suffers interference from copper. Crown ether based electrode has also been reported [657] in literature for zinc. It exhibited a working concentration range of 70 μ M - 0.1 M with a Nernstian slope of 29.5 mV/decade of activity. *Shamsipur et al.* [658] reported a zinc-selective sensor based on benzo substituted macrocyclic diaramides. An electrode based on 5,6,14, 15-dibenzo-1,4-dioxo-8,12-diazacyclopentadecane-5,14-diene showed response for zinc [659]. It has a working concentration range of 5μ M - 100 μ M in the pH range of 1.5-7.0.

Chelating ion-exchanger resins are found to possess specific selectivity for some metal ions and play an important role in separation processes. *Wardak et al.* [660] studied the properties on the ion selective electrode with a chelating pseudo-liquid membrane phase for Zn^{2+} determination. A porphyrin based potentiometric sensor for Zn^{2+} determinations was prepared by *Gupta et al.* [661]

Literature survey reveals that the first Ni-ISE was developed by *Pungor* and *coworkers* [662] using nickel-dimethyl glyoxime complex. Later on, heterogeneous membranes of nickel phosphate [663] in paraffin and silicone rubber, *bis*-2-(ethylhexyl) phosphate [664] in PVC and nickel complex of 1,4,8,11-tetraazacyclotetradecane [665] in araldite were used for preparing Ni^{2+} selective

electrodes. Chelating ion-exchange resin (1-hydroxy-2-naphthaldoxime-formaldehyde polymer) containing nitrogen and oxygen donor atoms are prepared and characterized by *Srivastava et al.* [666]. The resin behaved as a selective cheating ion-exchanger for some metal ions. The PVC based membrane electrodes for the resin showed a Nernstian response for Ni^{2+} over a wide concentration range ($2.94 \times 10^3 - 5.87 \times 10^3$ M) between pH 3.0 and 7.5. The electrode is found to possess adequate stability and specific selectivity with a response time of 10 s. The sensor can also be used in partially non-aqueous medium having a 35% (v/v) non-aqueous content.

Polyvinyl chloride based membrane of 4,4',4",4"'-21H,23H-porphine-5,10,10,15,20-terayl) tetrakis (benzoic acid) (TBAP) and 2,3,7,8,12,13,17,18-octamethyl-21H, 23H-porphine (OMP) were prepared using dibutylphthalate (DBP), dioctaylphthalate (DOP), dibutyl(butyl)phosphonate (DBBP) and 1-chloronaphthalene (CN) as plasticizing solvent mediators and sodium tetraphenylborate as an ion-excluder for Ni^{2+} selective sensor [667].

A PVC membrane nickel(II) ion-selective electrode was constructed by *Mousavi et al.* [668] using 1,10-dibenzyl-1,10-diaza-18-crown-6 (DBzDA18C6) as a neutral carrier. The sensor exhibited a Nernstian response for Ni(II) ions over a wide concentration range $5.5 \times 10^{-2} - 2.0 \times 10^{-5}$ M. It has a relatively fast response time and can be used for at least 6 weeks without any considerable divergence in potentials. The proposed sensor revealed relatively good selectivity for Ni(II) over a wide variety of other metal ions.

Pentacyclooctaaza have been explored as a neutral ionophore for preparing poly(vinyl chloride) (PVC)-based membrane sensors selective to Ni(II) [669]. The optimized membrane incorporating pentacyclooctaaza as the active material, dibutyl phthalate as plasticizer and sodium tetraphenyl borate as an anion excluder and membrane modifier in PVC in different ratio's was directly coated on the surface of a platinum-wire electrode. The electrode exhibited a near Nernstian response in the concentration range of 1×10^{-6} to 1×10^{-1} M Ni(II). The limit of detection, as determined from intersection of the extrapolated linear segments of the calibration graph, was 6×10^{-7} M. It has a response time between 5 and 40 s for nickel concentrations ranging from 1×10^{-1} to 1×10^{-6} M. The electrode revealed moderate selectivities over a number of alkali, alkaline earth and several transition and heavy metal ions. The electrode is suitable for use in aqueous solutions in a wide pH range of 3-6. It was applied as an indicator electrode for the end point detection in the potentiometric titration of Ni(II) with ethylenediaminetetraacetic acid (EDTA) and determination of nickel content of chocolate and milk powder samples.

Due to the vital importance of copper in many biological systems [670,671] and industry [672], the urgent need for a copper-selective electrode for potentiometric monitoring of Cu^{2+} in different industrial, medicinal and environmental samples, a variety of ion carriers have been used in the construction of copper(II) selective electrodes. These copper ion carriers include small size thiacrown ethers [673,674], non-cyclic neutral ionophores containing dithiocarbamate groups [675,676] and nitrogen atom [677], calix [673], arenes [678], Schiff's bases [677,678-681] and macrocycles di-amides [682] various species.

However, all of these copper sensors have one, two or in some cases, all of the following problems: (1) high detection limit, (2) narrow working concentration range and (3) serious interfering effect of cations such as Fe^{3+}, Na^{+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Cs^{+}, K^{+}, Hg^{2+}, Ag^{+}. Potentiometric measurements with a Cu^{2+} ion-selective electrode allow directly determining free ion concentration in water samples. For copper determination, solid membrane electrodes based on copper sulfide [683-686], tungsten oxide [687], ion-exchangers [688,689] and copper(III) complexes [690-695] as electroactive material have also been tried as copper potentiometric sensors. In order to obtain on macrocyclic polyethers [696,697] and polymethylidene [698] have been developed. *Talantsev* and *Syroratskaya* [699] determined Cu^{2+} potentiometrically by using ISEs with a crystal membrane, which is found to be more sensitive than the photometric method using diethylthiocarbamate. Comparative analyses were made with river water and the method has better characteristics than the photometric method and can be used for the analysis of natural and wastewaters. *Banes et al.* [700] have synthesized a novel highly copper(II) selective chelating ion-exchanger electrode based on poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) beads modified with aspartic acid derivatives.

A copper(II) ion-selective electrode based on copper(II) salicylaniline Schiff's base complex in styrene-co-acrylonitrile copolymer (SAN) has been developed by *Gupta et al.* [701]. The SAN-based membrane electrode containing copper(II)–Schiff's base complex, dioctylphthalate as plasticizer and sodium tetraphenylborate as an anion excluder exhibited a linear response with a Nernstian slope of 30 mV/decade within the concentration range of $1 \times 10^{-6} - 1 \times 10^{-2}$ M of Cu^{2+} ions. The

selectivity of electrode for Cu^{2+} ion has been found to be better in comparison to other various interfering ions. The prepared electrode can be used successfully as an indicator electrode for the potentiometric titration of the Cu^{2+} ion using EDTA. *Ganjali et al.* [702] have also reported a novel copper selective electrode by using a new Schiff's base bis-2-thiophenal propanediamine (TPDA) as an excellent neutral carrier for the potentiometric monitoring of ultra trace amount of Cu^{2+} ions. The membrane electrode was successfully used for the direct determination of copper in black tea and as an indicator electrode in potentiometric titration of copper ion.

Mashhadizadeh et al. [703] have prepared a new PVC membrane electrode that was highly selective for Cu(II) ions. The electrode was prepared by using 3,6,9,14-tetrathiabicyclo [9.2.1] tetradeca-11,13-diene as a neutral carrier. The electrode exhibited a Nernstian slope of 28 mV per decade change in concentration over a wide range i.e. 10^{-7} M Cu^{2+}.

Polypyrazolylmethanes, represented by the general formula $H_{4-n}C(pz)n$ (pz:1-pyrazolyl), form a six-membered MN_4C chelate ring of a shallow boat configuration, acting as tridentate or bidentate ligands. *Yoshimoto et al.* [704] developed novel ion-selective membrane electrodes based on polypyrazolylmethanes and report the first results of their use. $HC(pz)_3$ (1), $HC(3,5\ Me_2pz)_3$ (2), $HC(3\text{-}Phpz)_3$ (3), $HC(3\text{-}i\text{Prpz})_3$ (4), $HOCH_2C(pz)_3$ (5), and $C(pz)_4$ (6) were prepared as described in the literature and incorporated as an ionophore in PVC membrane. The selectivity of the electrodes changed with the substituents of polypyrazolylmethanes. The electrodes of 3,4 and 6 were selective for Cu^{2+} at pH 5.5. The electrode 4 showed rapid response time (~ 10 s) and reproducible results for more than 4 months, and successfully applied to

potentiometric titration of Cu^{2+} with EDTA. Recently, *Fakhari et al.* [705] reported a Cu(II) ion-selective membrane electrode based on 2,2'-[1,2-ethandiyl-bis(nitrilomethylidine)-bis]*meta* cresole(I), 2,2'-[1,2-ethandiyl-bis(nitrilomethylidine)-bis] *ortho* cresole(II), and 2,2'-[1,2-ethandiyl-bis(nitrilomethylidine)-bis] *para* cresole(III) as excellent neutral ion carriers.

In measuring the heavy metal ions like Cd^{2+} in the industrial wastewater, the ion-selective electrodes are very convenient because of simplicity and selectivity. *Ross et al.* [706,707] have reported the precipitate based solid state CdS-Ag_2S mixture membrane by stoichiometric reaction. Also, *Hirata et al.* [708] have developed the ceramic solid-state CdS-Ag_2S mixture membrane by baking the CdS-Ag_2S mixed powder or its pressed membrane at 700 °C. *Hopertenam* and *Cosma* [709] have reported some preparation methods for mixtures of cadmium and silver sulfides with Cd^{2+}-selective electrode properties. Sodium sulfide, thioacetamide and sodium thiosulfate were used for simultaneous precipitation of CdS and Ag_2S.

The selectivity of the Cd^{2+} ion-selective electrode is affected by Cu^{2+}, Pb^{2+} and Fe^{3+} ions co-existed in industrial wastewater. Also, it interfered by an oxidizer such as chlorine or hypochlorite ion. The detection limit and the calibration curve were slightly changed by pH of samples as in basic solutions Cd^{2+} ion becomes cadmium hydroxide $Cd(OH)_2$. In the acidic solution, the detection limit becomes inferior owing to the increasing of solubility of CdS. All sample measurements should be performed in the best pH region. Therefore, the buffer solution for Cd^{2+} ion measurement such as Orion TISAB (total ion strength adjustment buffer) [710] for the fluoride ion measurement, which could mask the interfering substances, was

developed for the practical use. *Loginova* and *Chernysheva* [711] have also reported the Cd^{2+}-buffer for potentiometry with ion-selective electrodes in miceller media.

Srivastava et al. [712] have reported a plasticized PVC based membrane of benzo-15-crown-5, which exhibited a good response for Cd^{2+} in a wide concentration range ($3.16 \times 10^{-5} - 1.00 \times 10^{-1}$ M) with a slope of 20 mV/decade of $[Cd^{2+}]$. The electrode was used at one stretch, for a period of 2 months and is played good selectivity for Cd^{2+} over alkali, alkaline earth and transition metal ions. The membrane sensor was also used as an indicator electrode in potentiometric titration involving Cd(II) ions. *Parez-Marin* and *coworkers* [713] have used 2-furoyl-3-benzyl-3-phenylthiourea, which was deposited on an epoxy resin and employed as neutral barrier for the ion detection of cadmium. The sensor exhibited a Nernstian slope of 29.8 mV/decade. Potential response of Cd(II) ion-selective electrode based on cyanocoplymer matrixes and 8-hydroxyquionoline as ionophore was evaluated by *Gupta* and *D'Arc* [714]. The cyano groups of the copolymers contributed significantly to enhance the selectivity of the electrode. The electrode showed an appreciable average life of 6 months without any significant drift in the electrode potential, which is explained considering phase boundary model based on thermodynamics considerations.

Shamsipur and *coworkers* [715] have developed a cadmium(II) ion-selective membrane electrode based on newly synthesized [1,1'-bicyclohexyl]1,1'2,2'-tetrol as membrane carrier. The proposed membrane sensor showed excellent discrimination ability towards Cd^{2+} ion with regard to several alkali, alkaline earth, transition and heavy metal ions. It was successfully applied for the direct determination of Cd^{2+} in

solution and as an indicator electrode in potentiometric titration of cadmium ions. *Singh et al.* [716] have reported a polystyrene based membrane of 3,4,12,13-dibenzo-2,5,11,14-tetraoxo-1,6,10,15-tetracyclooctadecane as a membrane carrier for Cd^{2+} ions. It was found that some amounts of surfactants do not disturb the functioning of the sensor and also used to estimate Cd^{2+} ions in real samples.

Because of the increased industrial use of lead, at one hand and its serious hazardous effect to human health, on the other [717], the electrochemical properties and preparation of the Pb(II) ion-selective membrane electrodes have been extensively studied by using different active materials. *Thind et al.* [718] have developed Pb^{2+} ion-selective membrane using lead antimonate as an electroactive phase and araldite as a polymer binder. *Khan et al* [314,315,355-357] have published their finding for the determination of Hg(II), Cd(II), Pb(II), by potentiometric titration using polypyrrole/polyantimonic, polyaniline Sn(IV) tungstoarsenate, polyaniline Sn(IV) arsenophosphate, polypyrrole Th(IV) phosphate, polyaniline Sn(IV) phosphate and poly-o-toluidine Zr(IV) phosphate electrically conducting organic-inorganic composite based ion-selective membrane electrodes.

Gupta et al. [719] have published their results on the studies of araldite based Zr(IV) tungstophosphate (ZWP) membrane as Pb(II) ion-selective electrode. ZWP is a cation-exchanger has been used as an electroactive phase. Besides the solid-state membranes [720-725,] and liquid ion-exchange membranes [726,727], there has been increasing interest to the use of ionophore ligands as sensing materials for neutral carrier type Pb(II) ion-selective electrodes, mainly due to the unique selectivities of

these compounds. Most of the about 20 Pb^{2+}-selective ionophores described so far have been characterized in ISEs [728].

In 1986 *Shpigun et al.* [729] used five macrocyclic ligands as Pb carriers in PVC membranes plasticized with 66% dioctylphthalate or o-nitrophenyl octyl ether. Dibenzo-18-crown-6 and diazadibenzo-18 crown-6 was found to be good carriers for Pb^{2+}-selective electrodes for potentiometry in solutions containing $2 \times 10^{-6} - 1 \times 10^{-2}$ M Pb(II) ions. In 1987, *Navikov et al.* [730] used dibenzo-18-crown-6 and 3,17-diazadibenzo-18-crown-6 as carriers for lead selective electrodes. Lead in environmental samples was determined using an ISE by *Li* and *Liu* [731]. In 1995, a PVC-based membrane of 15-crown-5 was used by *Srivastava et al.* [732] for a lead selective electrode. *Tavakkoli* and *Shamsipur* [733] had reported a Pb-ISE based on dibenzopyridino-18-crown-6 as membrane carrier. This lead selective electrode exhibited comparatively good selectivities with respect to alkali, alkaline earth and some transition and heavy metal ions. *Malinowska et al.* [734] have reported a lead selective membrane electrode containing ionophores based on diaza-18-crown-6 units possessing amide and sulfonamide functions. *Malinowska et al.* have also reported polymeric membrane ion-selective membrane electrodes based on thioamide functionalized calix[4] arenes for which the selectivity coefficients for Pb^{2+} relative to Cu^{2+} were 10^{-3}-10^{-4} [735]. While *Ohki et al.* [736] have made solvent polymeric membrane ISEs by using 12 kinds of N,N,-dialkylamide derivatives of the dibenzopolyether dicarboxylic acids as Pb^{2+} selective neutral carriers. Potentiometric slectivities of the ISEs for the Pb^{2+} over other heavy metal cations, alkali metal cations and alkaline earth metal cations have been assessed. Another Pb^{2+}-selective

membrane electrode based diaza-18-crown-6 was reported by *Mousavi et al.* [737]. They constructed a PVC membrane lead(II) ion selective electrode using 1,10-dibenzyl-1,10-diaza-18-crown-6 as membrane carrier. This electrode was employed as an indicator electrode in potentiometric titration of EDTA with lead ions and used for direct determination of lead in wastewater. *Bis*(2-ethylhexyl) phosphate is quite suitable for making a Pb^{2+} selective electrode. Thus an electrode constructed using *bis*(2-ethylhexyl) phosphate and *bis*(1-butylpentyl) adipate as a solvent mediator in a PVC membrane matrix showed high selectivity and sensitivity [727]. When (2-ethylhexyl) group was replaced by benzyl group, the sensitivity and selectivity to Pb^{2+} were considerably improved. Thus, *Xu and Katsu* [738] employed dibenzyl phosphate and *bis*(1-butylpentyl) adipate as a solvent mediator in a PVC membrane matrix exhibited a near-Nernstain response to Pb^{2+} in the concentration range from 3 $\times 10^{-6}$ to 1 $\times 10^{-2}$ M with a slope of 30.1 mV per concentration decade. They have also employed tetrabenzyl pyrophosphate and biphenyl phosphinic anhydride with two phosphoryl groups as liganding sites, which can be used as novel ionophores to make Pb^{2+}-selective membrane electrodes. A good result was obtained with tetrabenzylpyrophosphate and the electrode based on this ionophore and the electrode membrane matrix with PVC exhibited a near-Nernstian response to Pb^{2+} in the concentration range of 1 $\times 10^{-5}$ – 1 $\times 10^{-2}$ M with a slope of 28.7 mV/concentration decade in a solution containing 0.1 M $Mg(NO_3)_2$. Addition of potassium tetrakis(*p*-chlorophenyl) borate (40% mol relative to tetrabenzyl-pyrophosphate) caused a drastic change in the response slope (53.3 mV/concentration decade), probably due to

the formation of PbA^+, where A stands for anions present in the sample solution, and decreased significantly the electrode selectivity to other metal cations [739].

9,10-Anthraquinones are the largest group of natural quinines and have significant chemical importance. In addition to a wide variety of chemical and industrial applications [740], recently synthetic derivatives of anthraquinones have employed as a lead carrier in PVC membrane. *Shamsipur et al.* [741] used four different 9,10-anthraquinone derivatives to characterize their abilities as lead(II)-ion selective electrodes in PVC matrix membrane. The electrode based on 1,8-dihydroxy-2,7-*bis*(prop-2'-enyl)-9,10-anthraquinone exhibited a Nernstain response for Pb^{2+} ions over a wide concentration range ($2.0 \times 10^{-3} - 2.0 \times 10^{-6}$ M). Another 9,10-anthraquinone derivatives *e.g.*, *bis*[(1-hydroxy-9,10-anthraquinone)-2-methyl] sulfide [742] and 1,4-*bis*(prop-2'-enyloxy)-9,10-anthraquinone [743] have also been used as lead(II) membrane carrier.

The derivative of quinaldic acid, 8-(dodecyloxy-quinoline-2-carboxylic acid), was used as an ionophores in the development of a Pb(II) selective electrode by *Casado et al.* [744]. Solvent extraction studies showed that this compound is selective for Pb(II) and Cu(II) over a variety of divalent and monovalent metals. The electrode is selective for Pb^{2+} over Cu^{2+}, Al^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Na^+ and K^+ with Hg^{2+} and Cu^{2+} the most interfering metal ions. *Mousvi et al.* [745] studied a PVC-based capric acid membrane potentiometric sensor for lead(II) ions. The optimum composition of the membrane was 30 wt.% PVC, 60 wt.% NPOE as plasticizers, 5 wt.% ionophore and 5 wt.% potassium tetrakis(*p*-chlorophenyl)borate as lipophilic salt. The electrode was used for the potentiometric titration of chromate ions with Pb^{2+} ions.

Sadeghi and Shamsipur [746] has reported a PVC membrane electrode for Pb^{2+} ions based on tetraphenylporphyrin. The sensor exhibited a Nernstian response for Pb^{2+} ions over a wide concentration range ($1 \times 10^{-5} - 1 \times 10^{-2}$ M). The proposed electrode showed a fairly good discriminating ability towards Pb^{2+} ions in comparison to some alkali, alkaline earth, transition and heavy metals ions and was used as an indicator electrode in potentiometric titration of Pb^{2+} ions. They have also reported ion-selective membrane electrode for the determination of Pb^{2+} ions based on a non cyclic ion-carrier, piroxicam [747]. In competition to PbS-based Pb(II) electrodes, the piroxicam-lead(II) ISE demonstrated the advantage of virtually no interference from some common transition metal ions such as Fe^{3+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+} and only slight interference from alkaline earth metal ions is observed.

Ganjali et al [748] have employed 5,5'-dithiobis-(2-nitrobenzoic acid) as a suitable ion carrier to construct a lead selective electrode PVC based membrane which exhibited significantly high selectivity to lead ion over alkali, alkaline earth and several transition metal ions.

Ganjali et al. [749] have reported a PVC membrane electrode for Pb^{2+} ion based on recently synthesized dimethylbenzotetrathiafulvalene as membrane carrier. The electrode has found a very low limit of detection of 8×10^{-6} M and can be used as an indicator electrode in potentiometric titrations of Pb^{2+} ions in both H_2O and 90% MeOH solutions.

Kulapina et al. [750] proposed lead selective electrode from tetraphenyl borates of lead(II) complexes of polyhydroxyethylated nonylphenols with various number of hydroxyethyl groups. *Parez-Marin et al.* [751] studied the 1-furoyl-3-(2-

hydroxyethyl)thiourea as ionophores for lead(II) in electrode of liquid membrane of neutral carrier. This PVC polymeric membrane was deposited drop wise directly into a composite graphite-epoxy support. The sensor exhibited a Nernstian slope at 29.17 mV/decade and a linear response range between $4 \times 10^{-5} - 6.9 \times 10^{-3}$ M.

Isidak [752] has reported the solid state lead(II) ion selective PVC membrane electrode using dimethylene *bis*(4-methylpiperidinethiocarbamate) as a neutral ionophore and nitrophenyloctyl ether or dioctylsebacate as plasticizers. They found that the response properties of solid state contact PVC membrane electrode prepared with nitrophenyloctyl ether was better that those of the membrane electrode prepared with dioctylsebacate.

Ensaf et al. [753] have prepared the lead(II)-selective membrane electrode by incorporating cryptland(222) as the neutral carrier into a plasticized PVC membrane. The electrode was used as an indicator electrode in the potentiometric titration of Pb^{2+} with EDTA. In this connection, more recently they have also reported the use of 1-phneyl-2-(2-quinolyl)-1,2,-dioxo-2-(4-bromo) phenylhydrazone (PQDBP) as an excellent neutral carrier in construction of a lead-PVC membrane electrode [754]. The membrane electrode was also applied to the titration of Pb^{2+} solution with potassium chromate as well as determination of lead in mineral samples. *Vardhan* and *Singh* [755] have reported a lead(II)-selective electrode having a chelating ion-exchange resin (salicylaldoxime-formaldehyde polymer) containing nitrogen and oxygen donor atoms, as electroactive material. The characteristics of two ion-selective electrodes based on PVC and polystyrene membrane in the presence of interfering ion has been studied. The ion-exchange coefficients and diffusion of

Pb(II) in Nafion-modified electrodes were determined by *Liu et al.* [756] in the process of ion-exchange. *Yang et al.* [757] have reported the use of diazacrown ethers bearing double armede thenoyl and thipheneacetyl groups as potential selective agents for Pb^{2+} ion-selective membranes. Acyclic amides oxamides have also been investigated as potential inophores for lead [758,759]. *Kamata and Onoyama* [760,761] used acyclic dithiocarbamates as inophore for Pb^{2+} ion-selective electrodes. *Jabar et al.* [762] have introduced liquid ion-exchange membranes incorporating the tetraphenylborate salts of nonionic surfactant polyoxylates for the preparation of lead selective sensor. *Shamsipur et al.* [763] reported the use of hexathia-18-crown-6-tetraone (HT-18C6TO) as an excellent neutral carrier in construction of lead PVC membrane electrode. *Ganjali et al.* [764] introduced a high selective and sensitive lead ion selective membrane coated on a graphite (CGISE) for potentiometric monitoring of ultra trace amount of Pb^{2+} in environment samples by using N,N,- dimethylcyanodiaza-18-crown-6 (DM-CDA18C6) as an excellent ionophore. *Jeong et al.* [765] described the fabrication and characterization of new lead ion-selective electrode based on *N,N'*-bis(salicylidene)-2,6-pyridinediamine as an ionophore. The coordinating effect for the selective response of lead ion was also investigated by using PVC membrane.

Lee at al. [766] have reported the lead(II)-selective electrodes based on porphyrin atropisomers tetrakis(2-hydroxy-1-naphthyl). The membrane electrode displayed a good Nernstian response (29.2 mV/decade) to Pb^{2+} over the linear range of 3.2×10^{-5} to 1×10^{-1} M. Most of metal ions would not affect the selectivity of the lead electrode seriously. *Jain et al.* [767] studied in detail a comparative study of

Pb^{2+}-selective sensors based on the membrane of 2,12-dimethyl-7,17-diphenyltetrapyrazole (I) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (II).

Mahajan et al. [768] reported a mercury ion selective electrode based on the *p*-tert-butyl calix[4] crown derivatives with imine units as an inophore. The electrode exhibited a good response for mercury(II) ions over a concentration range of 5.0×10^{-5} - 1.0×10^{-1} M with a near Nernstian slope of 27.3 mV per decade. The electrode showed high selectivity for Hg(II) ions over most of the alkali, alkaline earth and transition metal ions. Fe^{3+} and Ag^{+} ions were found to be the interfering ions. *Mashhadizadeh et al.* [769] reported the use of Schiff base ligand recently synthesized in his laboratory [770] of bis[5-((4-nitrophenyl)azo salicylaldehyde)](BNAS) as an excellent neutral carrier in construction of mercury(II)-PVC membrane electrode. The electrode was utilized as a potentiometric sensor for the titration of mercury(II) solution with EDTA.

Gupta et al. [771] reported the electroanalytical applicability of a diamine donor ligand as mercury ion sensor. The results presented in this paper showed that the sensor developed for Hg(II) ion using the above system as electroactive phase in a PVC matrix has a wide working concentration range and a fast response time with reproducible results.

The construction, performance, and applications of coated-wire mercury(II) selective electrodes based on 2-mercaptobenzimidazole (MBIM) and hexathiacyclooctadecane (HT18C6) carriers, in plasticized PVC matrix, were described by *Mazloum et al.* [772]. The influences of membrane composition and pH on the potentiometric response of the electrodes were investigated. The electrodes

exhibit near Nernstian responses for Hg^{2+} ions over a wide concentration range (4 to 5 decades of the concentration), and a detection limit of about 6×10^{-7} M. The response time of the electrodes is between 20 and 100 s, depending on the concentration of mercury, and they can be used for about 2 months without any considerable divergence in potential. The proposed sensors revealed good selectivity for Hg^{2+} in the presence of several metal ions. The best selectivity was observed for the electrode based on MBIM carrier. They were used as indicator electrodes in the potentiometric titration of Hg^{2+} with EDTA and for the determination of mercury in wastewater samples.

Mahajan et al. [773] reported mercury(II) ion-selective electrode based on alicylaldehyde thiosemicarbazone (I) as an ionophore. Thiosemicarbazones are an important class of ligands with enormous biochemical applications [774]. The electrode exhibited high selectivity for mercury(II) ions over alkali, alkaline and some transition metals (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Ag^+). This is the first report on use of a thiosemicarbazone as ionophore for metal ions [775-777]. The membrane electrode was also applied in the titration of Hg^{2+} with I^{-1} ion.

Lu at al. [778] reported the hitherto unknown selective complexation of the (1-thiazole) azo-functionalized calix[6]arene derivative as a novel ionophore used in a mercury ion-selective PVC membrane electrode. In this work, the effect on the response of changing the acidity and the anionic site and the response characteristics of the electrode produced were investigated. The results showed that the proposed electrode could be applied in real samples.

Dithiazone [779], dithia crown ethers [780], hexathia-18-crown-6-tetraone [781] and 2-mercaptobenzimidazole were also used as potential selective agents for Hg^{2+} PVC membrane electrodes having a good Nernstian response and high ion selectivity. Recently, 1,3-diphenylthiourea [782] has been reported as a very selective ionophore for the Hg^{2+} ISE, but the applicability has not been described.

Mercury (II) ion-selective PVC membrane sensor based on ethyl-2-benzoyl-2-phenylcarbamoyl acetate (EBPCA) as novel nitrogen containing sensing material was developed by *Hassan et al.* [783]. The sensor exhibited good linear response of 30 mV per decade within the concentration range $1 \times 10^{-6} - 1 \times 10^{-3}$ M Hg(II). The sensor shows good selectivity for mercury(II) ion in comparison with alkali, alkaline earth, transition and heavy metal ions. The proposed sensor was also applied as a sensor for the determination of Hg(II) content in some amalgam alloys. *Jain et al. and Srivastava et al.* have also fabricated polystyrene supported heterogeneous ion-exchange membrane electrode of heteropolyacid salts (*e.g.* Ce(IV) selenite), which were found to be selective for Hg^{2+}. Recently, *Abbas et al.* [784] have reported a new triiodomercurate-modified carbon paste electrode for the potentiometric determination of Hg(II) ions. Potentiometric determination of Hg(II) was also reported by some other workers [785-787].

Potentiometric membrane sensors for uranium(IV) were commonly prepared using phosphate esters [788-790], phosphites [791], phosphine oxides [792], diphosphine oxide [793], acyclic oligoethers with terminal phosphonate groups [794], butyl calixarene [795] and macrocyclic [796] ionophores. Bifunctional chelating agent O-methyldihexylphosphine oxide O'-hexyl-2-ethyl phosphoric acid

has also been proposed as a single molecular unit which combines the overall properties of the synergetic properties of phosphine oxide and ester of phosphoric acid [797] and has been used as an electroactive material in a membrane sensor. Hydroxy-acetophenone oxime-thiourea-trioxane resin [798], dihydroxy propiophenone oxime formaldehyde resin [799], tertiary ion association complexes of uranyl ion with ethylviolet-benzoic acid [800] and binary complexes with 2-thenoyl trifluoroacetone [801] have also been used in polymeric membrane based uranyl sensors. Many of these sensors, however, suffer from the disadvantages of a narrow range of response [794], interference from associated anions [788,799] and some common cations [796,798] and the need for several time consuming steps for ionophore preparation [798,799,802].

Although bis(ethylhexyl) phosphate ester (BEHP) has been used in PVC membrane sensors responding to uranyl ions [788], the more lipophilic derivative tris(ethylhexyl)phosphate (TEHP) has never been examined. On the other hand, a literature survey showed that O-(1,2-dihydro-2-oxo-1-pyridyl)- *N,N,N',N'* bis(tetramethyl)uranium hexafluorophosphate (TPTU) has no analytical applications despite the presence of four active chelating centers in its structure [803]. Both reagents are commercially available and are used either as a solvent or as a peptide-coupling agent. Therefore, DTP A and TPTU reagents were examined by *Hassan et al.* [804] as novel ionophores in PVC based membrane sensors for uranyl ions. Sensors with optimized membrane composition displayed enhanced selectivity, stability, fast and linear response for a wide concentration range of uranyl ion.

Characterization and applications of these sensors for quantification of uranium in certified and naturally occurring ores are also described.

A less attention has been made for determining tripositive metal ions. Very few potentiometric devices have been designed for aluminum [805-809]. *Saleh et al.* [810] have reported a novel potentiometric membrane sensor for selective determination of Al(III) ions. In this PVC matrix membrane sensor incorporating 7-ethylthio-4-oxa-3-phenyl-2-thioxa-1,2 dihydropyrimido[4,5]pyrimidine ionophore has been used as membrane carrier for Al^{3+} ions. This electrode has a minimum interference of Pb^{2+} and Hg^{2+} ions and successfully applied for the potentiometric titration of HPO_4^{2-} with Al^{3+} and for direct potentiometry of Al^{3+} content of some rock samples. A novel Fe(III)-selective PVC membrane electrodes based on formylsalicyclic acid derivatives were also reported by *Saleh* [809]. Fe^{3+} ion-selective membranes sensor based on the use of coated wire anionic membrane incorporating tetrachloroferrate(III)-aliquate suffered from significant interference from many cations such as Sn^{2+}, Hg^{2+} and Zn^{2+} [811]. These difficulties also arise on using a heterogeneous solid-state cation-exchanger membrane with stannic arsenate dispersed in epoxy resin [812]. *Volkov et al.* [813] have developed a Fe(III) selective solid phase electrode with an ion-sensitive material Fe(III) metavanadate.

A literature survey revealed that very little work has been done on the development of ISEs for Cr(III) ion, the first report on Cr(III) was in 1980 [814], in this study a PVC based chromium(III)-wire electrode was made by incorporating (Aliquat $336S^+$–$Cr(SCN)_4^-$) ion pair, and the electrode gave a fully linear response in the $Cr(SCN)_4^-$ concentration range of 10^{-5}–10^{-2} M and has the Nernstian slope of 58

mV per decade of Cr(III) concentrations.

In 1983 [815], a Cr(VI) selective electrode with PVC membrane based on triheptyldodecylamonium iodide was described. The response of the electrode was Nernstian for Cr(VI) concentration down to 2×10^{-6} M in 0.03–0.13 M HF solution with limit of detection of 5×10^{-7} M. In 1984 [816], PVC matrix membrane Cr(VI) selective electrodes based on ethyl violet or victoria blue were prepared at pH 3.5 and in concentration range of $2.5 \times 10^{-5} - 1 \times 10^{-1}$ M of Cr(VI). The detection limit of this electrode was 1.1×10^{-5} M.

In 1987 an ion selective electrode for determination of chromium(III) was reported. In this electrode 8-quinoline-dithiocarboxylate was used as a membrane-active substance [817]. In 1989 an ion-selective electrode based on chromium dithizonate was built that was a precipitate based selective electrode [818]. Almost 10 years ago it was estimated that more than 7000 papers on ISEs had been published [819]. Numerous ISEs based on PVC membrane were reported for many inorganic ions [820], but very little was published on PVC-based trivalent ions. A PVC-based Cr(III) ion selective electrode which was recently been prepared is based on a macrocyclic compound with a concentration range of $1.77 \times 10^{-6} - 0.1$ M and a Nernstian slope of 20 mV per decade [821]. *Abbaspour* and *Izadyar* [822] reported a PVC matrix ion selective electrode for chromium(III), which is based on 4-dimethylaminoazobenzene with a concentration range of $1.66 \times 10^{-6} - 1 \times 10^{-2}$ and limit of detection 8.0×10^{-7} M and also possessed the advantages of simplicity of the design in membrane preparation.

A poly(vinyl chloride) membrane based on glyoxal bis(2-hydroxyanil) as membrane carrier was prepared by *Gholivand et al.* [823] and investigated as a Cr(III)-selective electrode. The electrode has a linear dynamic range of $3.0 \times/10^{-6}$-$/1.0 \times 10^{-2}$ M with a Nernstian slope of 19.89 mV per decade and a detection limit of $6.3 \times/10^{-7}$ M. It has a fast response time of 20 s and can be used for at least 3 months without any considerable divergence in potential. The membrane sensor has been used very successfully for the analysis of some food materials and alloys for the determination of Cr(III) ion. A polystyrene based membrane of tetraazacyclohexadeca-1,4,9,12-tetraene macrocyclic ionophore was used as Cr(III) ion-selective electrode by *Singh et al.* [824]. The electrode has been found to be chemically inert and of adequate stability with good reproducibility over a period of 100 days. The membrane electrode worked satisfactorily in a partially non-aqueous medium upto a maximum 30% (v/v) content of methanol and ethanol. The selectivity coefficient values indicated that the membrane electrode is highly selective for Cr(III) ions over a number of monovalent, diavalent and trivalent cations.

Few reports on Ce(III)-selective electrodes based on 1,2,3-trithiane [825,826] sulfonamide [827], azomethine of pipronylidine-4-[2.2]paracyclophenylamine [828] and aminobenzothiazol [829] as ionophores were developed as sensors for Ce(III) ions. The selectivity coefficients recorded by these electrodes showed interferences of some cations such as Hg(II) and Fe(III).

A novel ion-selective PVC membrane sensor for cerium(III) ions based on [4-(4'- nitrobenzyl)-1-phenyl-3,5-pyrazolidinedion)] (NBPP) as a new ionophore has been prepared and studied by *Saleh et al.* [830]. This electrode has a wide linear

dynamic range from 10^{-1} to 2.5×10^{-6} M with a Nernstian slope of 29.5 mV per decade and low detection limit of 1.6×10^{-6} M. It has a fast response time (<10 s) and good selectivity with respect to different metal ions. The proposed electrode has also been used successfully as an indicator electrode in potentiometric titration of phosphate and oxalate in aqueous media and carbonate, fluoride and acetylsalicylate in some drugs.

1.8.4. Applications of ion-exchanger based membranes and ion-selective electrodes

The membrane separation technology occurred more than a quarter century ago when *Srinivasa Sourirajan*, a physical chemist working at the University of California, Los Angeles, announced the development of the first synthetic symmetric membrane that could be used for "surface skimming" of sea water or brackish water for the production of pure water by ion-exchange membranes. Besides these, the membrane technology has been in practice in water treatment to provide potable water. Neosepta type ion-exchange membranes prepared by *Mizutani et al.* [831] were used mainly for chemical utilization of desalination of seawater in Japan.

Recently, polymer based inorganic ion-exchanger membranes have become a research target because the exchangers act as an electroactive phase and polymers (*i.e.*, cellulose acetate, polysulfone, polypropylene, polyvinylidene, regenerated cellulose, polyacrylonitrile, polyamide, polycarbonate, organic conducting polymers, *etc.*) provide binding support to these material to shape into membrane. These membranes are being investigated towards their employment as biosensors, chemical

sensors and ion-selective electrodes. These ion-exchange membranes having some charge over them therefore may be utilized for the recovery of selective ionic species from industrial effluents in better way and may be helping tool to solid waste management. Thus, ion-exchange membranes have been extensively employed in various applications *i.e.*, in fuel cells, acid recovery, stabilization baths, such as aluminum anodizing, steel pickling *etc.*, substitution reactions-adjustment of acid in juice production of inorganic and organic chemicals, chloralkali cells, electro-dialysis, purification of H_2SO_4 and HCl, recovery of HNO_3 and HF, extraction of transition metals by using liquid ion-exchange membranes, and in a number of environmental pollution abatement processes like solid waste management, *etc.*

Nowadays, many efforts have been taking to improve the method of preparations of different kind of ion-exchange membranes. Recently, *Towe* and *Yagar* [833] have reported the different method of manufacture and its uses of ion-exchange membrane. *Terada et al.* [834] prepared polyolefin based heterogeneous ion-exchange membranes with low electrical resistivity and high mechanical strength comprising ion-exchange resins (*e.g.*, Diaions SK-18, Diaion SA-10A), and binder polymers containing LDPE and EPR or EPDM.

Sata [835] reviewed with 24 references on the preparation of the composite ion-exchange membranes. The composite membranes have applications to lithium battery, ferric and ferrous ion redox cell and humidity sensors. While *Sengupta et al.* [836] made the selective removal of heavy metals from sludges or soil using composite ion-exchange membranes. *Xu et al.* [837] manufactured the ion-exchange membranes with microporous polypropylene having a thickness of 15-50 μm.

Wang et al. [838] made the selection of inorganic ion-exchangers for removing cesium. They studied the properties of five series and twenty types of inorganic ion-exchangers for removing Cs(I) from acidic high-level radioactive liquid waste. The results showed that $Ti[Fe(CN)_6]/K_4[Fe(CN)_6]$ prepared by sol-gel technique had high mechanical property, excellent ion-exchange property and their selection as the ion-exchanger for removing Cs(I) from high level radioactive liquid waste. *Xu et al.* [839] also reviewed with 37 references on the development and applications of ion-exchange membranes in the treatment of industrial wastewaters.

Determination of Ca^{2+} and Mg^{2+} by potentiometric titration using ion-selective electrode as the indicator electrode, and EGTA and EDTA as the titrants were reported by *Fang* and *Dan* [840]. The method was used to determine the amount of Ca^{2+} and Mg^{2+} in mineral water and silicate samples with satisfactory results. Similarly, *Agarwal et al.* [841] determined the water hardness directly by using Mg(II) ion-selective electrodes comprising Mg(II)-N-phenylbenzohydroxamate complex as an electroactive material. This membrane electrode exhibited almost equal selectivities for Ca^{2+} and Mg^{2+}, thus can be used for the simultaneous determination of both ions. Recently, Gupta *et al.* [842] have also reported the amount of hardness of water using heterogeneous inorganic ion-exchanger based Mg(II)-selective electrode. *Stephen et al.* [843] used the immobilized molten salt membrane based magnesium sensor for aluminum-magnesium melts. The activity of magnesium in the aluminum-magnesium melt was determined with respect to a pure magnesium reference contained in the inside of the thimble and sealed from the surrounding atmosphere and melt by zirconia based cement. Measurements were

conducted in various commercial aluminum-magnesium alloys under inert atmosphere as well as in air.

A short review on the application of membrane technology in food technology has been reported in the literature [844]. *Lee et al.* [845] investigated many PVC membrane electrodes for the determination of basic drugs like chlorpromazine, amityline, nortiptyline, *etc. Wen et al.* [846] have reported a methylene blue PVC membrane electrode based on methylene blue-phosphotungstate ion pair complex as electroactive material and its successful use in the determination of methylene blue in injection. A good agreement for the results of methylene blue content in injection between the potentiometric method and the United State Pharmaceutical standard procedure are found. An anticancer drug *e.g.*, tetracycline hydrochloride was successfully determined by using both coated wire and the conventional polymer membrane types electrodes by *Issa et al.* [847]. These electrodes are based on incorporating the tetracycline-phosphotungstate ion association in plasticized PVC film. Recently, *Sirkar* [848] reviewed the application of membrane technologies in the pharmaceutical industry with 29 references. This review covers the most recent application of membrane technologies in blood range of separation, concentration and purification needs. A number of technologists and scientists have also found the new areas to employ the ion-selective electrodes in various types of analyses of blood, plasma serum and of surfactants.

A heterogeneous membrane in which Zr(IV) tellurite gel was embedded in polystyrene and used to prepare an electrode that was used by *Srivastava et al.* [849] for the estimation of Cr(IV) in water, and in tannery and plating wastes. Recently,

Pareau et al. [850] have developed a novel procedure for purification of liquid industrial effluents by eliminating the heavy metals ions. In this, an emulsion liquid membrane extraction process was developed to recover lead and cadmium from industrial effluents. The best carrier was found to be the Cyanex 301 or a mixture of cyanex 301 and Aliquat 336. Similarly, *Pradelle* and *Cueille* [851] focused on the inorganic membrane-innovation process for the chemical industries.

Zhou et al. [852] determined the aluminum powder content of propellent powder (Type-71-25) with a fluoride ion-selective electrode. *Sakurai et al.* [853] determined the Fe(III) ion concentration in acidic solution for the treatment of steel, stainless steel and special steel by using a copper ion electrode or a redox electrode. Similarly, *Ion et al.* [854] have reported the potentiometric determination of Fe(III) in fertilizers using ion-selective electrode with liquid membranes, which is based on the complex crystal violet-tetrachloroferrate(III). *Li* and *coworkers* [855] have reported the fast determination method of free calcium in human milk with ion-selective electrode. *Wang* [856] have developed the principle and method for determining the lime concentration in soil with pH glass electrode and PVC membrane calcium ISE. The neutral carrier ETH 1001 is used as the electroactive material for the calcium ion-selective electrode.

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Chapter 2

Preparation and characterization of new and novel 'organic-inorganic' composite cation-exchange materials: polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate

Chapter 2

2.1. Introduction

Organic polymers as ion-exchangers are well known for their uniformity, chemical stability and control of their ion-exchange properties through synthetic methods [1]. The inorganic ion-exchange materials based on polyvalent metals have been established now an excellent recognition in various disciplines, *i.e.* metal ion separation, preconcentration, catalysis, environmental studies, medical science (kidney dialysis), ion-selective electrodes preparation, heterogeneous solid state membranes formation and in ion-exchange fibers preparation, *etc.* Besides other advantages, these materials are important in being more stable to high temperature and radiation field than the organic ones [2].

In order to obtain a combination of these advantages associated with organic and inorganic materials as ion-exchangers, attempts have been made to develop a new class of composite ion-exchangers by incorporation of electrically conducting organic polymers (polyaniline, polypyrrole, polythiophene *etc.*) into the matrices of inorganic precipitates of multivalent metal acid salts.

Composite materials formed by mixing organic polymers and inorganic particles; possess all the good properties of both the constituents and an enhanced utility thereof. The combination of organic and inorganic precursors yields hybrid materials that have mechanical properties not present in the pure materials. The organic group can be reactive which implies that it is able to form an organic network

as well as inorganic network. In designing composite materials scientists and engineers have ingeniously combined various metals, ceramics, and polymers to produce a new generation of extraordinary materials that encompass a wide variety of applications. Most composites have been created to improve combination of mechanical characteristics such as stiffness, toughness, and ambient and high temperature strength. Of particular interest is the molecular level combination of two different components that may lead to new composite materials that are expected to provide many possibilities termed 'organic-inorganic hybrid' materials [3-7] with better chemical, mechanical, and thermal stabilities, reproducibility and possessing good selectivity for heavy metals indicating its useful environmental applications. Thus, inorganic precipitate ion-exchanger based on organic polymeric matrix must be an interesting material, as it should possess the mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger regarding its selectivity towards some particular metal ions.

Many 'organic-inorganic' composite ion-exchangers have been developed earlier by incorporation of organic monomers into inorganic matrix, by way of pillaring or non-pillaring methods [8-12]. Few such excellent ion-exchange materials have been developed in our laboratory and successfully being used in environmental analysis [13-27].

Due to the conductivity in the semiconductor region, organic-inorganic composites prepared with electrically conducting polymers have emerged as fascinating materials due to a wide range of other desirable properties such as

architectural flexibility, environmental stability, ease of fabrication, light weight, mechanical property and so on. Therefore, these materials are finding applications from coating to lubricants to solid-state technology to biotechnology. Conducting polymers possess good tunable electrical conductivity and are organic electrochromic materials with chemically active surface [28,29]. But they are chemically sensitive and have poor mechanical properties and thus pose a processibility problem. On the other hand, inorganic oxides or metal acid salts show the presence of more sites for surface reactivity and are highly porous in solution form. The metal oxides constitute a class of compounds widely used as cathode material in Li-ion batteries [30]. They also have good mechanical properties and are good dispersants too [31]. Recently, several groups have combined conductive polymers with metal oxides to generate hybrid composites that possess higher reversible ion capacity, and structural stability [32-36]. The properties of composites of such kind are strongly dependent on concentration of polymer. Polypyrrole, polyaniline and derivatives of polyaniline conducting polymers, have received a lot of attentions in the preparation of composites due to high stability of these polymers in conducting oxidized form [13,15,22,23,27,37-42].

In this regard, a number of 'organic-inorganic' composite cation-exchanger samples of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate were prepared by mixing polypyrrole and poyaniline into inorganic precipitate gels of thorium(IV) phosphate and tin(IV) phosphate, respectively under varying conditions. In order to determine the composition, structural and thermal properties of these

materials several physico-chemical investigations were carried out by elemental analyses, atomic absorption spectrophotometry (AAS), scanning electron microscopy (SEM), spectral analyses (FTIR), thermal analyses (simultaneous TGA-DTA) and X-ray analyses. Their thermal stabilities were studied at various temperatures and chemical stabilities were assessed in various acidic, alkaline and organic media. This chapter presents the preparative conditions and physico-chemical properties of these composite materials.

2.2. Experimental

2.2.1. Chemicals and reagents

The main reagents used for the synthesis were:

- Thorium nitrate, $Th(NO_3)_4.5H_2O$ (99 %) — CDH (India)
- Phosphoric acid, H_3PO_4 (88-93 %) — Loba Chemie (India)
- Pyrrole, C_4H_4NH (98%) — E-Merck (India)
- Toluene, $C_6H_5CH_3$ (95%) — CDH (India)
- Ferric chloride, $FeCl_3$ (96%) — CDH (India)
- Aniline, $C_6H_5NH_2$ (99%) — Qualigens (India)
- Potassium persulphate, $K_2S_2O_8$ (98%) — CDH (India)
- Stannic(IV) chloride, $SnCl_4.5H_2O$ (97.5%) — CDH (India)
- Di-sodium hydrogen orthophosphate, Na_2HPO_4 — CDH (India)
- Nitric acid, HNO_3 — E-Merck (India)
- Hydrochloric acid, HCl (35%) — E-Merck (India)

All other reagents and chemicals were of analytical reagent grade.

2.2.2. Instrumentation

The following instruments were used for various studies made for chemical analysis and characterization of the composite materials:

- A digital pH meter — Elico (India), model LI-10; was used for measuring pH.
- UV/VIS spectrophotometer — Elico (India), model EI 301E; was used for quantitative analysis.
- Double beam atomic absorption spectrophotometer (AAS) — GBC 902 (Australia) with air-acetylene flame; was used for the quantitative determination of Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}.
- A digital flame photometer — Elico (India), model CL 22D; was used for the

quantitative determination of Na^+, K^+, Ca^{2+}.

- ❖ A scanning electron microscope — LEO 435 VP (Australia) with attached imaging device; was used to examine the difference in surface morphology between the parent materials and their composites.
- ❖ FTIR spectrometer — Perkin Elmer (U.S.A.), model Spectrum BX; was used for recording FTIR spectra.
- ❖ Elemental analyzer — Elementra Vario EL III, Carlo-Erba, model 1108; was used for C, H and N analyses.
- ❖ A thermal analyzer — V2.2A DuPont 9900; was used for simultaneous TGA (thermogravimetric analysis) and DTA (differential thermal analysis) studies.
- ❖ An X-ray diffractometer — Phillips (Holland), model PW 1148/89 with Cu Kα radiations; was used for recording powder X-ray diffraction pattern.
- ❖ An automatic temperature controlled water bath incubator shaker — Elcon (India).
- ❖ A digital muffle furnace — was used to heat the material at different temperatures.
- ❖ An air oven — Labquip (India).
- ❖ An electronic balance (digital) — Sartorius (Japan), model 21 OS; was used for weighing purpose.
- ❖ A magnetic stirrer.
- ❖ A mortar pastel.

2.2.3. Preparation of organic-inorganic composite cation-exchange materials

2.2.3.1. Preparation of reagent solutions

0.1 M solutions of thorium nitrate, $Th(NO_3)_4.5H_2O$ and stannic chloride, $SnCl_4.5H_2O$ were prepared in 1 M HNO_3 and 4 M HCl, respectively, while

orthophosphoric acid, H_3PO_4 solutions of different molarities, 0.1 M di-sodium hydrogen orthophosphate, Na_2HPO_4 and 0.1 M $FeCl_3$ solutions were prepared in demineralized water (DMW). Pyrrole solution of 33.33% concentration (v/v) was prepared in toluene. Solutions of 10% (v/v) doubly distilled aniline ($C_6H_5NH_2$) and 0.1 M potassium persulphate ($K_2S_2O_8$) were prepared in 1 M HCl.

2.2.3.2. Synthesis of polymer

2.2.3.2.1. Synthesis of polypyrrole

It is well known that polypyrrole can be easily synthesized through electrochemical oxidative polymerization of pyrrole and that is an excellent conductive polymer [43,44]. On the other hand, pyrrole can be polymerized through chemical oxidative polymerization using suitable oxidizing agents, such as ferric chloride [45], quinones [46], potassium peroxidosulphate [47] and ozone [48]. In this endeavor, polypyrrole samples were prepared when approximately 33.33% solutions of pyrrole (in toluene) were added drop wise to the 0.1 M $FeCl_3$ solutions (prepared in DMW) in different volume ratios at room temperature with continuous stirring by a magnetic stirrer. Black colored flakes of polypyrrole samples were obtained.

2.2.3.2.2. Synthesis of polyaniline

Polyaniline is typically synthesized by oxidizing aniline monomer either electrochemically [49,50], chemically [51-53], plasma polymerization [54], autocatalytic polymerization [55] and inverse emulsion polymerization [56]. Electrochemically synthesized polyaniline is difficult to process due to its low

solubility, while chemically synthesized polyaniline suffers from low molecular weight, which results in low mechanical strength [57]. In recent years, considerable effort has been devoted to developing new methods to synthesize polyaniline to achieve better mechanical properties, while maintaining high conductivity. The most common strategy that has been implemented is to change the oxidizing agent employed in the chemical polymerization reaction [57-59]. Thus, the oxidative polymerization of aniline in aqueous acidic media by a variety of oxidizing agent *viz.* ammonium persulphate ($(NH_4)_2S_2O_8$), potassium persulphate ($K_2S_2O_8$), potassium dichromate ($K_2Cr_2O_7$), cerium sulfate ($Ce(SO_4)_2$), sodium vanadate ($NaVO_3$), potassium ferricyanide ($K_3(Fe(CN)_6)$), potassium iodate (KIO_3), hydrogen peroxide (H_2O_2) are recommended [60,61]. While the most commonly used oxidizing reagents are persulphates in aqueous HCl [62,63]. In this study, polyaniline gels were prepared by mixing different volumes of the acidic solutions of 10% aniline ($C_6H_5NH_2$) and 0.1 M potassium persulphate with continuous stirring by a magnetic stirrer below 10 °C for half an hour. Green colored polyaniline gels were obtained and kept overnight in a refrigerator.

2.2.3.3. Synthesis of inorganic precipitate

2.2.3.3.1. Synthesis of thorium(IV) phosphate

The method of preparation of the inorganic precipitate of Th(IV) phosphate ion-exchanger was very similar to that of Alberti and Constantino [64], with slight modification [65] by mixing a solution of 0.1 M $Th(NO_3)_4.5H_2O$ prepared in 1 M HNO_3 at the flow rate of 0.5 ml min^{-1} to a solution of H_3PO_4 in different molarities.

Constant stirring was done during mixing using a magnetic stirrer at a temperature of 85 ± 5 °C, white gel type slurries were obtained. After digestion of the mixture for several hours, it was cooled to room temperature in each case.

2.2.3.3.2. Synthesis of Sn(IV) phosphate

Inorganic precipitates of Sn(IV) phosphate were prepared at room temperature (25 ± 2 °C) by adding 0.1 M stannic chloride ($SnCl_4.5H_2O$) solutions prepared in 4 M HCl to aqueous solutions of 0.1 M di-sodium hydrogen orthophosphate (Na_2HPO_4) in different mixing volume ratios. The white precipitates were obtained, when the pH of the mixtures was adjusted to 1 by adding aqueous ammonia with constant stirring.

2.2.3.4. Preparation of organic-inorganic composites

2.2.3.4.1. Preparation of polypyrrole thorium(IV) phosphate composite cation-exchanger

0.1 M $FeCl_3$ solutions were mixed thoroughly with the inorganic precipitate of Th(IV) phosphate, to which approximately 33.33% solutions of pyrrole in toluene were added drop wise, continuous stirring was done during the addition of pyrrole solution, slowly the white inorganic precipitate gels turned first to green and then to black. The reaction mixtures were kept for 24 hours under ambient condition (25 ± 2 °C). Now the polypyrrole based composite gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ferric chloride. The washed gels then dried over P_4O_{10} at 30 °C in an oven. The dried products were immersed in DMW to obtain small granules. They were converted to the H^+-form by

keeping it in 1 M HNO_3 solution for 24 hours with occasional shaking intermittently replacing the supernatant liquid with a fresh acid. The excess acid was removed after several washings with DMW. The materials were finally dried at 40 °C and sieving to obtain particles of particular size range (~125 μm). Hence a number of 'polypyrrole Th(IV) phosphate' composite samples were prepared (Table 2.1) and on the basis of Na^+ ion-exchange capacity (I.E.C.), percentage of yield and physical appearances, sample S-5 was selected for further studies.

2.2.3.4.2. Preparation of polyaniline Sn(IV) phosphate composite cation-exchanger

The gels of polyaniline were added to the white inorganic precipitates of Sn(IV) phosphate and mixed thoroughly with constant stirring. The resultant green colored gels were kept for 24 h at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was decanted and gels were filtered by suction. The excess acid was removed by washing with DMW and the material was dried in an air oven at 50 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H^+-form by treating with 1 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and the dried at 50 °C. The particles size of range (~ 125 μm) of the material was obtained by sieving and kept in desiccators.

Hence, a number of samples of 'polyaniline Sn(IV) phosphate' composite cation-exchanger were prepared (Table 2.2) and on the basis of Na^+ ion-exchange capacity, percentage of yield and physical appearance of beads, sample T-7 was selected for detailed studies.

Table 2.1

Conditions of preparation and the ion-exchange capacity of polypyrrole Th(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratios (v/v)					Appearance of the beads after drying	Na^+ ion exchange capacity (meq dry g^{-1})
	0.1 M $Th(NO_3)_4.5H_2O$ in 1 M HNO_3	H_3PO_4	Digestion time (h)	$FeCl_3$ (0.1 M)	Pyrrole in toluene (33.33%)		
S-1	5	2 (1 M)	4	2	0.30	Blackish granular	1.19
S-2	5	2 (1 M)	24	2	0.30	Blackish granular	0.78
S-3	5	3 (1 M)	4.30	2	0.30	Blackish granular	1.10
S-4	5	2 (2 M)	24	2	0.30	Blackish granular	0.62
S-5	5	2 (2 M)	5	2	0.30	Blackish granular	1.56
S-6	5	2 (2 M)	5	-	-	White sheet	0.72
S-7	-	-	-	2	0.30	Black powder	0.05
S-8	5	2 (2 M)	5	2	0.18	Blackish granular	0.58
S-9	5	2 (2 M)	5	2.5	0.42	Blackish granular	0.27
S-10	5	2 (2 M)	5	2.5	0.60	Blackish granular	0.29
S-11	5	2 (2 M)	5	2.5	0.75	Blackish granular	0.51
S-12	5	2 (2 M)	5	2.5	0.90	Blackish granular	0.31

Table 2.2

Conditions of preparation of various samples of polyaniline Sn(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratios (v/v)					Appearance of the beads after drying	Na^+ ion- exchange capacity (meq dry g^{-1})
	0.1 M $SnCl_4.5H_2O$ in 4 M HCl	0.1 M Na_2HPO_4 in DMW	pH of the inorganic precipitate	0.1 M $K_2S_2O_8$ in 1 M HCl	10% Aniline in 1 M HCl		
T-1	1	1	1.0	1	1	Greenish granular	1.10
T-2	1	2	1.0	1	1	Greenish granular	1.45
T-3	2	1	1.0	1	1	Greenish granular	0.85
T-4	2	2	1.0	1	1	Greenish granular	0.96
T-5	-	-	-	1	1	Greenish granular	0.20
T-6	2	3	1.0	-	-	White granular	1.12
T-7	2	3	1.0	1	1	Greenish granular	1.96
T-8	1	3	1.0	1	1	Greenish granular	0.58
T-9	1	4	1.0	1	1	Greenish granular	0.45
T-10	3	4	1.0	1	1	Greenish granular	0.72
T-11	2	3	1.0	2	1	Greenish granular	1.20
T-12	2	3	1.0	1	2	Dark green	0.98
T-13	2	3	1.0	2	2	Dark green	1.40
T-14	2	3	1.0	3	2	Dark green	0.92
T-15	2	3	1.0	2	3	Dark green	0.85

2.2.4. Physico-chemical properties of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchange materials

2.2.4.1. Chemical dissolution

Two hundred and fifty milligrams (250 mg) portions of the original (as prepared) form of both composite cation-exchangers (polypyrrole Th(IV) phosphate, S-5 and polyaniline Sn(IV) phosphate, T-7) were treated with 20 ml each of different acids (such as HCl, HNO_3, H_2SO_4, $HClO_4$, etc.), bases (such as NaOH, KOH, NH_4OH,), salt ($NaNO_3$, CH_3COONa, NH_4NO_3); organic solvents (such as dimethyl sulphoxide (DMSO), acetone, *n*-butyl alcohol, formic acid and citric acid) and also with DMW for 24 hours with occasional shaking. The supernatant liquids were analyzed for 'thorium' and 'tin' by atomic absorption spectrometer, while phosphates were determined as usual by the phosphovanado molybdate method [66] as described below. The results are summarized in Table 2.3 and Table 2.4.

2.2.4.1.1. Determination of phosphorous

2.2.4.1.1.1. Preparation of reagent solutions

2.2.4.1.1.1.1. Ammonium vanadate solution

2.5 g of ammonium vanadate (NH_4VO_3) was dissolved in 500 ml hot water, followed by the addition of 20 ml concentrated nitric acid and dilute with water to 1 L in a graduated flask.

2.2.4.1.1.1.2. Ammonium molybdate solution

50 g of ammonium molybdate [$(NH_4)_6 Mo_7O_{34}. 4H_2O$] was dissolved in warm

Table 2.3

Chemical stability of polypyrrole Th(IV) phosphate in various solvents

Solvent used (20 ml)	Amount dissolved (mg/20 ml)	
	Th(IV)	Phosphorus
DMW	0.00	0.25
1 M HCl	0.12	1.88
2 M HCl	0.35	2.62
4 M HCl	Completely dissolved	
1 M HNO_3	0.27	1.55
2 M HNO_3	0.69	3.12
4 M HNO_3	Completely dissolved	
0.5 M H_2SO_4	0.93	7.54
2 M H_2SO_4	Completely dissolved	
1 M $HClO_4$	0.23	2.02
2 M $HClO_4$	0.62	3.55
4 M $HClO_4$	Completely dissolved	
0.1 M KOH	0.07	1.04
0.1 M NaOH	0.06	0.84
1 M NH_4OH	0.04	1.50
1 M $NaNO_3$	0.00	0.38
10% Dimethylsulphoxide (DMSO)	0.00	0.21
Acetone	0.00	0.22
n-Butyl alcohol	0.01	0.45

Table 2.4

Chemical stability of polyaniline Sn(IV) phosphate in various solvents

Solvent used (20 ml)	Amount dissolved (mg/20 ml)	
	Sn(IV)	Phosphorus
DMW	0.00	0.150
1 M HCl	0.04	0.965
2 M HCl	0.04	1.542
4 M HCl	0.04	1.672
1 M HNO_3	0.04	0.930
2 M HNO_3	0.04	1.333
4 M HNO_3	0.34	1.546
1 M H_2SO_4	0.05	0.863
2 M H_2SO_4	0.05	0.425
4 M H_2SO_4	0.06	0.841
1 M Formic acid	0.06	1.942
1 M Citric acid	0.05	0.756
1 M CH_3COOH	0.05	1.347
0.1 M KOH	0.00	1.020
0.1 M NaOH	0.00	0.783
1 M CH_3COONa	0.00	0.312
1 M NH_4NO_3	0.02	0.985
10% Dimethylsulphoxide (DMSO)	0.11	1.860
Acetone	0.05	0.512
n-Butyl alcohol	0.07	1.423

water and diluted to 1 L in a graduated flask, filtered the solution before use.

2.2.4.1.1.2. Procedure

Ten milliliter of the supernant liquid was taken in a 25 ml volumetric flask, add 2 ml of (2:1) (nitric acid:DMW) solution followed by the addition of 2 ml of ammonium vanadate solution, and 2 ml of the ammonium molybdate solution, diluted to the mark and mixed thoroughly. The absorbance was recorded at 465 nm against a blank solution prepared in the same manner, using 1 cm cell. A series of standard solution of di-sodium hydrogen orthophosphate covering the range, 100-1000 ppm phosphorous per 100 ml was prepared containing the same concentration of acid, ammonium vanadate and ammonium molybdate as the previous solution. The amount of phosphorous was determined by using a standard curve drawn as per the same procedure by taking known amount of phosphorous.

2.2.4.2. Heat treatment

To study the effect of drying temperature, 1 g samples of the composite cation-exchange materials (S-5 and T-7) were heated at various temperatures in a muffle furnace for 1 hour each; and physical appearances and the percentage of weight losses were determined after cooling them at room temperature as shown in Table 2.5.

2.2.4.3. Chemical composition

The chemical composition also plays an important role in the elucidation of molecular structure of the ion-exchangers. The composition of the material can be

Table 2.5

Thermal stability of polypyrrole Th(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7) after heating to various temperatures for 1 h

Polypyrrole Th(IV) phosphate (S-5)			Polyaniline Sn(IV) phosphate (T-7)	
Heating temperature (°C)	Appearance (Color)	Weight loss (%)	Appearance (Color)	Weight loss (%)
40	Blackish brown	-	Greenish	-
100	Blackish brown	9.34	„	8.60
150	Blackish brown	12.15	„	14.12
200	Blackish brown	13.46	„	16.50
300	Black	19.26	Dark green	20.00
350	Black	25.07	Black	22.13
400	Black	30.80	Blackish brown	23.42
500	Light gray	39.42	Slightly white	32.64
600	Light gray	43.91	White	34.00

determined either by gravimetrically or spectrophotometrically. With the help of these methods, we can determine the percentage of metals or groups present in the ion-exchangers.

To determine the chemical composition of polypyrrole Th(IV) phosphate (Sample S-5, original form) and polyaniline Sn(IV) phosphate (Sample T-7, original form), two hundred mg of the each cation-exchanger were dissolved in 20 ml of concentrated H_2SO_4. The materials were analyzed for 'thorium(IV)' and 'tin(IV)' by ICP-MS and phosphate by the phosphovanado molybdate method as described above. Carbon, hydrogen and nitrogen contents of the cation-exchangers were determined by elemental analysis. The weight percent compositions of the material are presented in Table 2.6.

2.2.4.4. Scanning electron microscopy (SEM) studies

Microphotographs of the original form of organic polymers [polypyrrole (S-7), polyaniline (T-5),] inorganic precipitates [Th(IV) phosphate (S-6), Sn(IV) phosphate (T-6)] and organic-inorganic composite materials [polypyrrole thorium(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7)] were obtained by the scanning electron microscope at various magnifications.

2.2.4.5. X- ray analyses

Powder X-ray diffraction (XRD) patterns were obtained in aluminum sample holder for the sample S-5 (polypyrrole Th(IV) phosphate) and sample T-7 (polyaniline Sn(IV) phosphate) in the original form using a PW, 1148/89 based diffractometer with Cu, Kα radiations.

Table 2.6

Percent composition of polypyrrole Th(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7) composite cation exchangers

S. No.	Polypyrrole Th(IV) phosphate (S-5)		Polyaniline Sn(IV) phosphate (T-7)	
	Element	Percentage	Element	Percentage
1	Th	30.793	Sn	17.2
2	P	9.622	P	14.25
3	C	18.794	C	10.08
4	H	3.340	H	3.46
5	N	5.080	N	2.06
6	O	32.371	O	52.95

2.2.4.6. Fourier transform infra red (FTIR) spectroscopic studies

The FTIR spectrum of polypyrrole (sample S-7), Th(IV) phosphate (sample S-6) and polypyrrole Th(IV) phosphate (sample S-5) and polyaniline (sample T-5), Sn(IV) phosphate (sample T-6), polyaniline Sn(IV) phosphate (sample T-7) in the original form dried at 50 °C were taken by KBr disc method at room temperature.

2.2.4.7. Thermogravimetric analyses-differential thermal analyses (TGA-DTA) studies

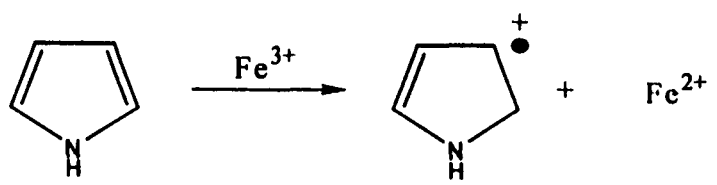
Simultaneous TGA and DTA studies of the composite cation-exchange materials (polypyrrole thorium(IV) phosphate, S-5 and polyaniline Sn(IV) phosphate, T-7) in original form were carried out by an automatic thermobalance on heating the material from 10 °C to 900 °C at a constant rate (10 °C per minute) in the air atmosphere (air flow rate of 200 ml min^{-1}).

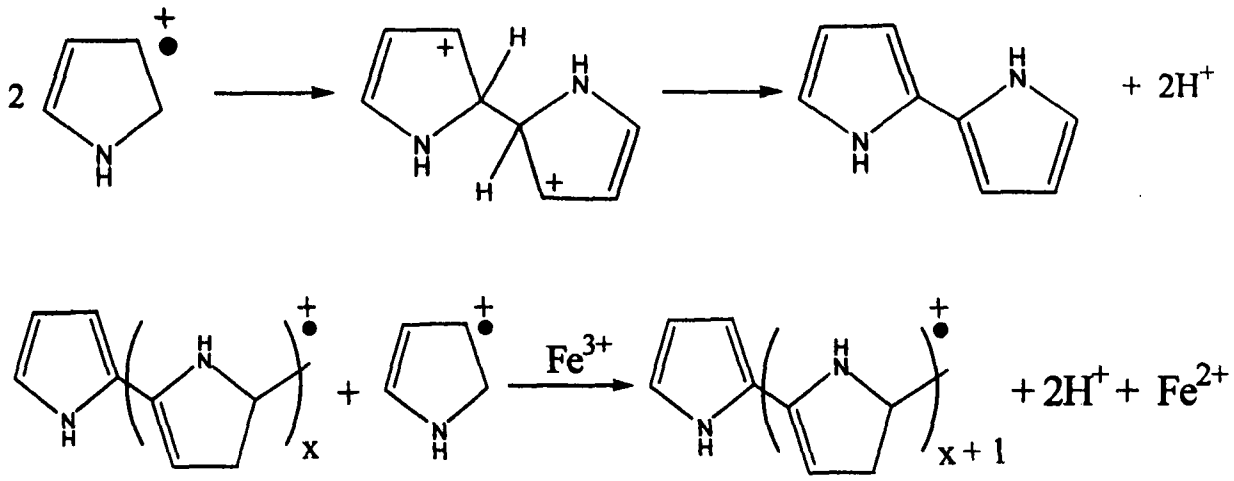
2.3. Results and Discussions

2.3.1. Preparation of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers

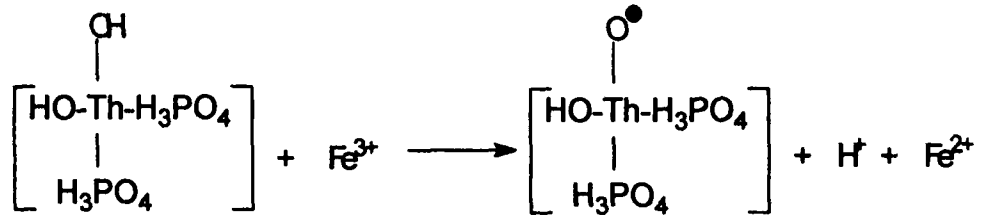
In this study of the preparation and characterization of 'organic-inorganic' composite cation-exchange materials a number of samples of 'organic-inorganic' electrically conducting composite cation-exchangers, polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate providing a new class of hybrid ion-exchangers were prepared by the sol-gel mixing of organic conducting polymers *i.e.* polypyrrole and polyaniline into the inorganic precipitate of Th(IV) phosphate and Sn(IV) phosphate, respectively by changing the mixing volume ratios. Among them, sample S-5 (Table 2.1) possessed better Na^+ ion-exchange capacity (1.56 meq dry g^{-1}) as compared to Th(IV) phosphate (0.72 meq dry g^{-1}) and sample T-7 (Table- 2.2) also possessed good Na^+ ion-exchange capacity (1.96 meq dry g^{-1}) as compared to Sn(IV) phosphate (1.12 meq dry g^{-1}), high percentage of yields, chemical, mechanical and thermal stabilities.

The polymerization reaction for the synthesis of polypyrrole is very complicated one. The initial oxidation step, in which a radical cation is formed, is followed by a coupling reaction, deprotonation, and one-electron oxidation in order to regenerate the aromatic system [67], using $FeCl_3$ in aqueous medium at room temperature (25 ± 2 °C) as given in the following reactions:

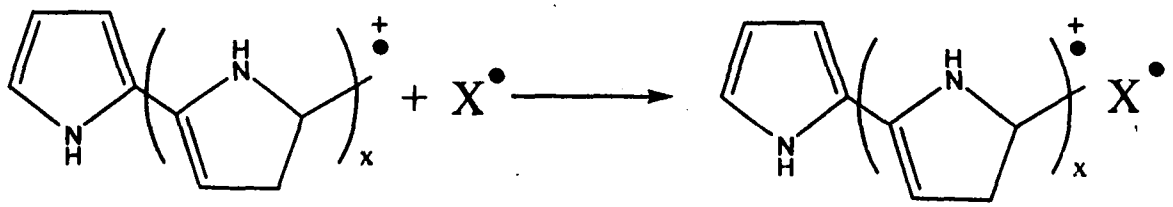




When aqueous solution of $FeCl_3$ was added with the inorganic precipitate of thorium(IV) phosphate, Fe^{3+} may convert thorium phosphate into a radical that can be shown as:

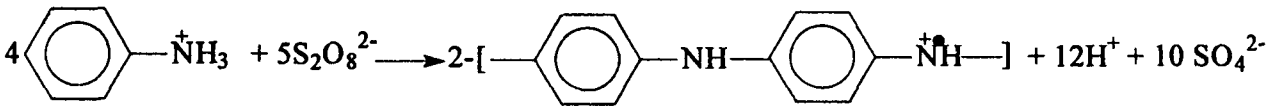


Hence, the binding of polypyrrole into the matrix of thorium(IV) phosphate can be shown as:



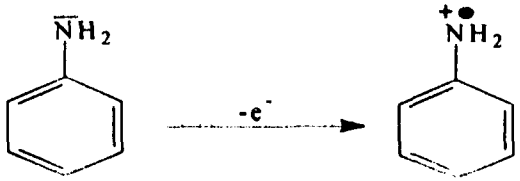
Polypyrrole Thorium(IV) phosphate Polypyrrole Th(IV) phosphate matrix

Polyaniline gel was prepared by oxidative coupling using $K_2S_2O_8$ in acidic aqueous medium as given in the following reaction [68]:

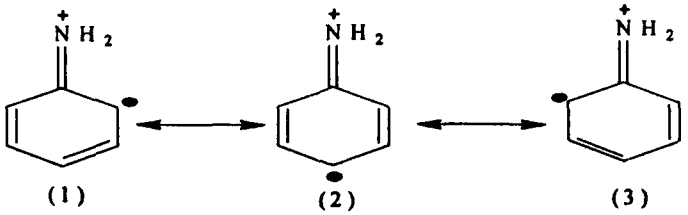


The various methods of polyaniline synthesis induce a multitude of polymerization mechanisms of aniline. The electrochemical polymerization mechanism seems to be the most investigated compared to the chemical one [69]. However, a close similarity can be considered for chemical and electrochemical processes [70].

The synthesis mechanism corresponds to a polycondensation because it proceeds by steps. The first most probable oxidation step corresponds to the radical cation formation by an electron transfer from the 2 s energy level of the aniline nitrogen atom as shown below:

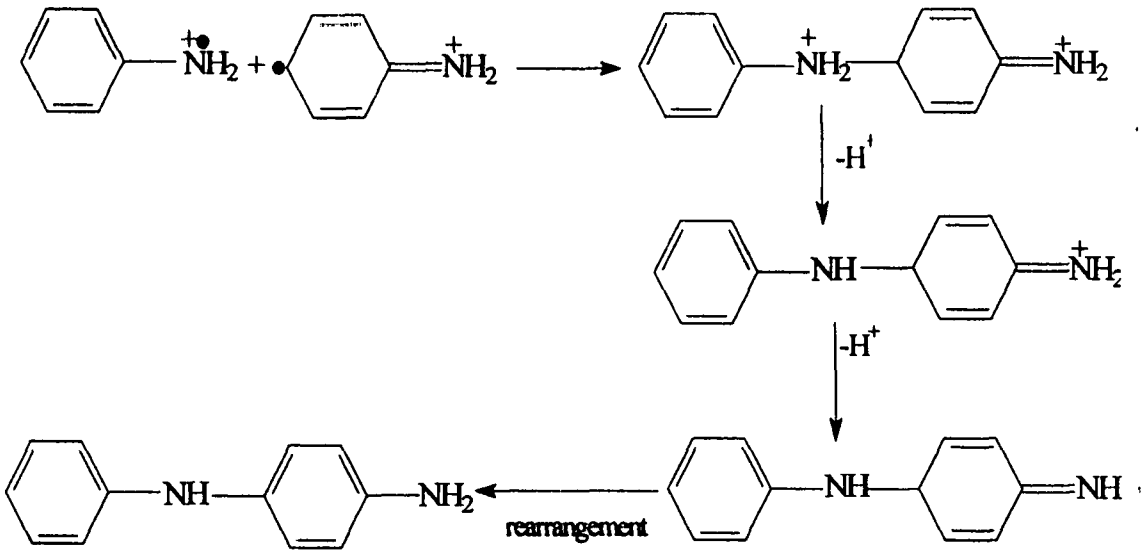


Above aniline cation radical has three resonance forms as given below:



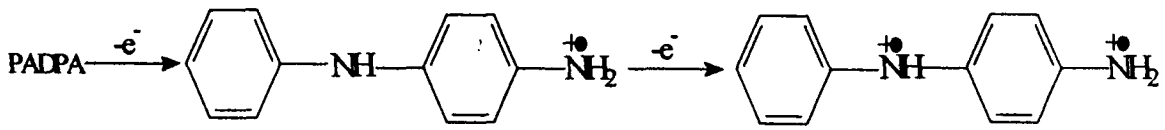
Among these three resonance forms, the form (2) is the more reactive one because of its important substituant inductive effect and on the other hand, of its absence of steric hindrance.

The next step, at the least in acidic medium, would be the reaction between the radical cation and the resonance form (2), the so-called "head to tail" reaction, favored in acidic medium (aqueous or organic) and corresponds to the dimer formation [70] as given below:

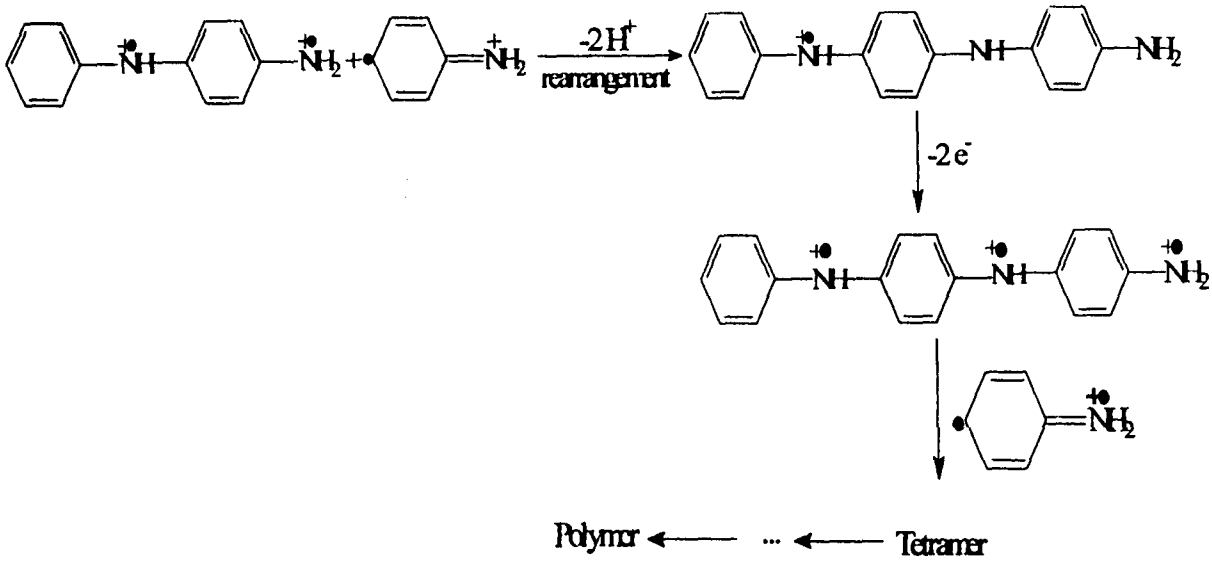


para-aminodiphenylamine (PADPA)

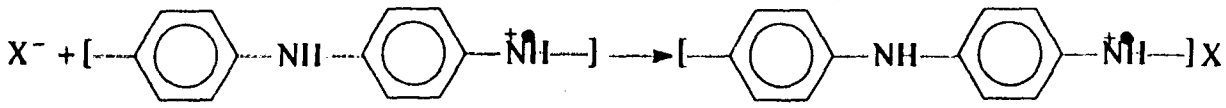
Next the dimer is oxidized to form a new radical cation, as shown below:



Above formed radical cation can react either with the radical cation monomer or with the radical cation dimer to form a trimer or a tetramer, respectively, according to the mechanism proposed previously, and this upto the polymer as given below:



The effect of temperature on the reaction seems to be very pronounced. Aniline under went oxidative coupling only at below 10 °C very effectively, leading to a good quantity of polyaniline with fairly good yield. The formation of inorganic precipitate of polyaniline Sn(IV) phosphate was significantly affected by the pH and the most favorable pH of the mixture was ~ 1.0. The binding of polyaniline into the matrix of Sn(IV) phosphate can be as:



Sn(IV) phosphate Polyaniline Polyaniline Sn(IV) phosphate matrix

However, sample S-5 of polypyrrole Th(IV) phosphate and sample T-7 of polyaniline Sn(IV) phosphate exhibited granulometric and mechanical properties, showing a good reproducible behavior as is evident from the fact that these materials obtained from various batches did not appreciable deviation in their percentage of yield and ion-exchange capacities.

2.3.2. Chemical stability

The chemical and thermal degradation of the matrix of ion-exchanger is the most important cause of decline the ion-exchangers. These two properties depend chiefly on the structure of the ion-exchangers, the degree of cross-linking of the matrix, and on the nature and number of the fixed ionic groups. Most of the resins present are stable in common solvents, except in the presence of strong oxidizing or reducing agents. The solubility experiment of polypyrrole Th(IV) phosphate composite cation-exchanger (Table 2.3) showed that the material has reasonable good chemical stability as the results indicated that the material was resistant to 2 M HCl, 2 M HNO_3, and 0.5 M H_2SO_4. This material is completely dissolved in 4 M HCl, 4 M HNO_3, 4 M $HClO_4$, and 2 M H_2SO_4. The chemical dissolution in DMW, alkaline media, $NaNO_3$, NH_3, DMSO, acetone and *n*-butyl alcohol was almost negligible. While the solubility experiment of polyaniline Sn(IV) phosphate (Table 2.4) showed that the material has reasonable good chemical stability as the results indicated that the material was resistant to solutions of different acid, bases, organic solvents, salts *etc*. The chemical dissolution in DMW, alkaline media, CH_3COONa, NH_4NO_3, was almost negligible. The chemical stability of both the composite cation-exchangers may be due to the presence of binding polymer, which can prevent the dissolution of heteropolyacids sols or leaching of any constituent element into the solution.

2.3.3. Thermal stability

It was observed that on heating at different temperatures for one hour, the

mass and physical appearance of the dried sample materials (S-5 and T-7) were changed as the temperature increased as shown in Table 2.5. Both the materials were found to possess higher thermal stability as the sample S-5 (polypyrrole Th(IV) phosphate) maintained about 69% of the initial mass by heating upto 400 °C, while sample T-7 (polyaniline Sn(IV) phosphate) maintained about 67% of the initial mass by heating upto 500 °C.

2.3.4. Scanning electron microscopy (SEM) studies

Scanning electron microscopy (SEM) studies were performed to examine the difference in surface morphology between the parent materials and their composites. SEM photographs of the polypyrrole (S-7), inorganic precipitate of thorium(IV) phosphate (S-6) and polypyrrole Th(IV) phosphate (S-5) and polyaniline (T-5), Sn(IV) phosphate (T-6) and polyaniline Sn(IV) phosphate (T-7) obtained at different magnifications (Fig. 2.1 and Fig. 2.2), indicating the binding of inorganic ion-exchange material with organic polymer, *i.e.* polypyrrole and polyaniline, respectively.

The SEM pictures of both the materials showed the difference in surface morphology of organic polymer, inorganic precipitate and composite material. It has been revealed that after binding of polypyrrole with Th(IV) phosphate and polyaniline with Sn(IV) phosphate, the morphology has been changed.

2.3.5. X- ray studies

The X-ray powder diffraction pattern of polypyrrole Th(IV) phosphate cation-

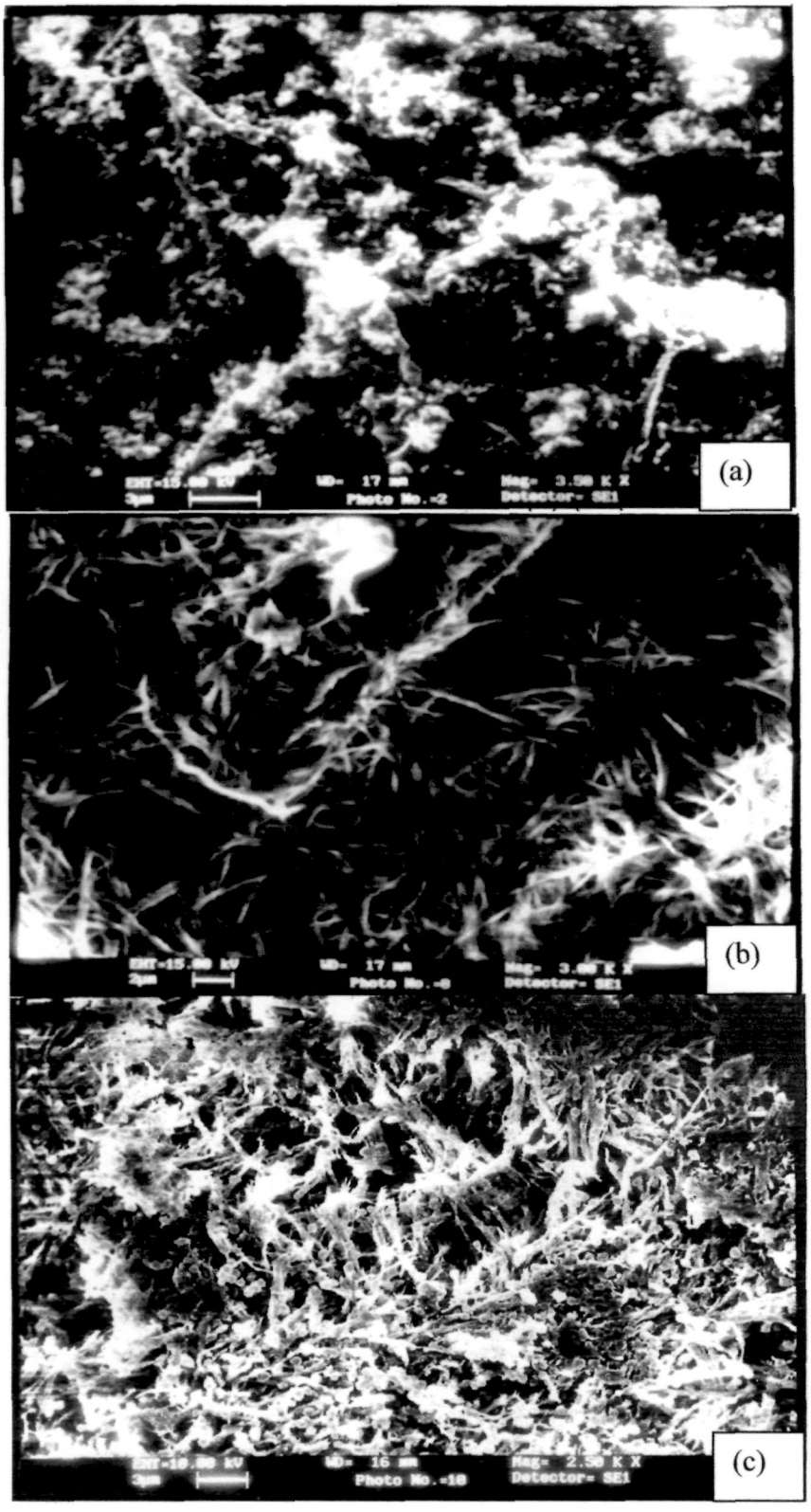


Fig. 2.1. Scanning electron microphotographs (SEM) of chemically prepared polypyrrole at the magnification of 3500 × (a), Th(IV) phosphate at the magnification of 3000 × and (b) and polypyrrole Th(IV) phosphate composite system at the magnification of 2500 × (c).

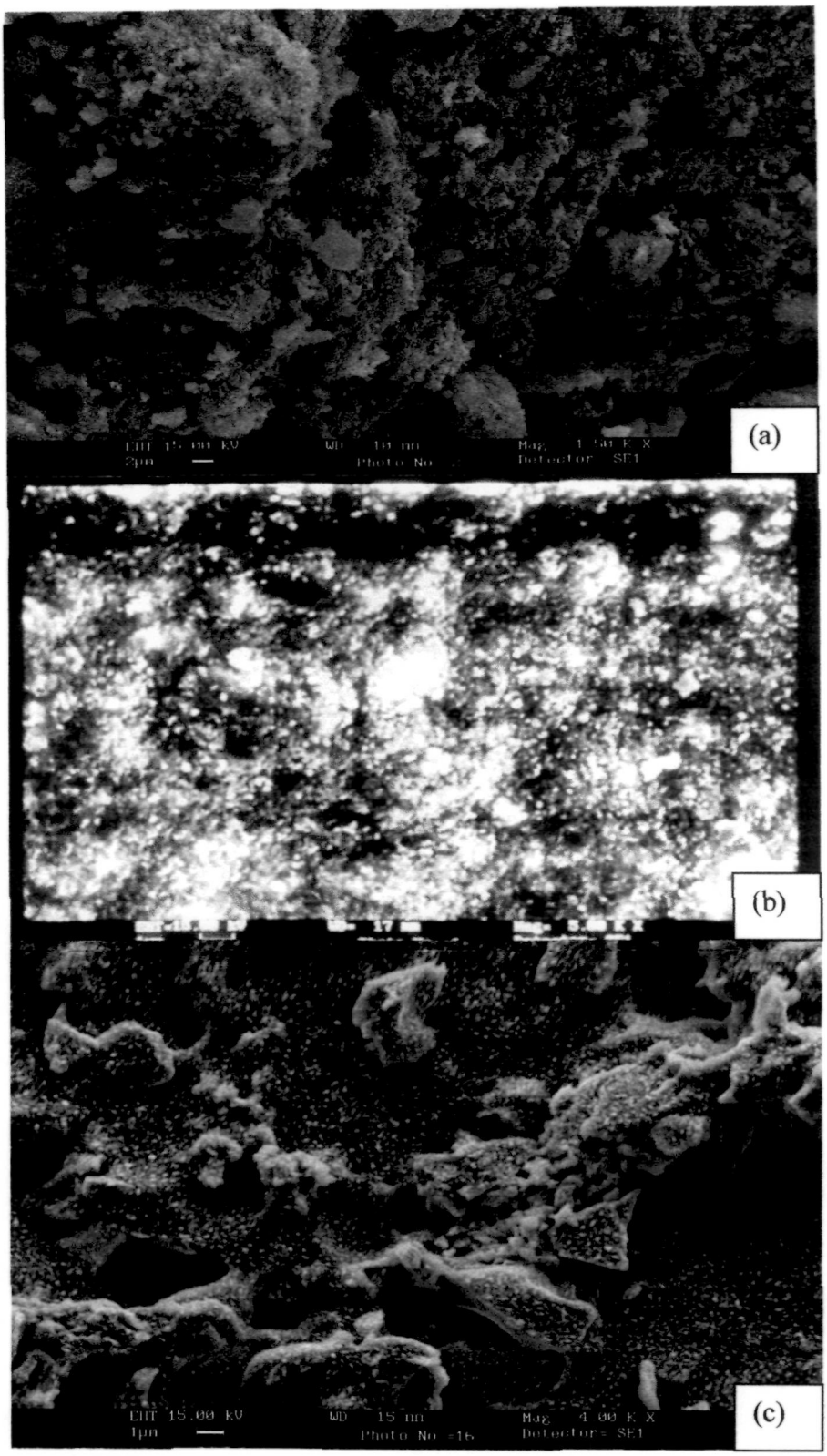


Fig. 2.2. Scanning electron microphotographs (SEM) of chemically prepared polyaniline at the magnification of 1500 × (a), Sn(IV) phosphate at the magnification of 5000 × and (b) and polyaniline Sn(IV) phosphate composite system at the magnification of 4000 × (c).

exchanger (sample S-5, as-prepared) recorded on powdered sample exhibited no peak in the spectrum (Fig. 2.3) that suggesting an amorphous nature of the composite material, while X-ray diffraction pattern of the polyaniline Sn(IV) phosphate composite cation-exchanger (sample T-7 as prepared) showed very small peaks of 2 0 values. The analysis of these small signal peaks support towards its semi-crystalline nature (Fig. 2.4).

2.3.6. Fourier transform infra red (FTIR) spectroscopic studies

The FTIR spectra of polypyrrole (a), thorium(IV) phosphate (b) and polypyrrole Th(IV) phosphate (c) are shown in Fig. 2.5 and the spectral peak positions are presented as tabulated form in Table 2.7. The FTIR spectrum of the composite cation-exchanger, sample S-5 (Fig. 2.5c) indicates the presence of extra water molecule in addition to the – OH groups and metal oxides present internally in the material. In the spectrum a strong broad band around 3400 cm^{-1} found which could be attributed to – OH stretching frequency. The peak at the 1647 cm^{-1} may be due to interstitial water present in the composite material [71]. An assembly of three peaks at 980-1080 cm^{-1} may represent the presence of ionic phosphate groups [72] in the material. The additional band at about 1400 cm^{-1} can be ascribed to stretching vibration of C-N [73]. This indicates that the material contains considerable amount of pyrrole.

Figure 2.6 shows the FTIR spectrum of polyaniline (a), Sn(IV) phosphate (b), and polyaniline Sn(IV) phosphate (c) and tabulated form of the spectral peak positions are presented in Table 2.8. It is evident from the FTIR studies of the

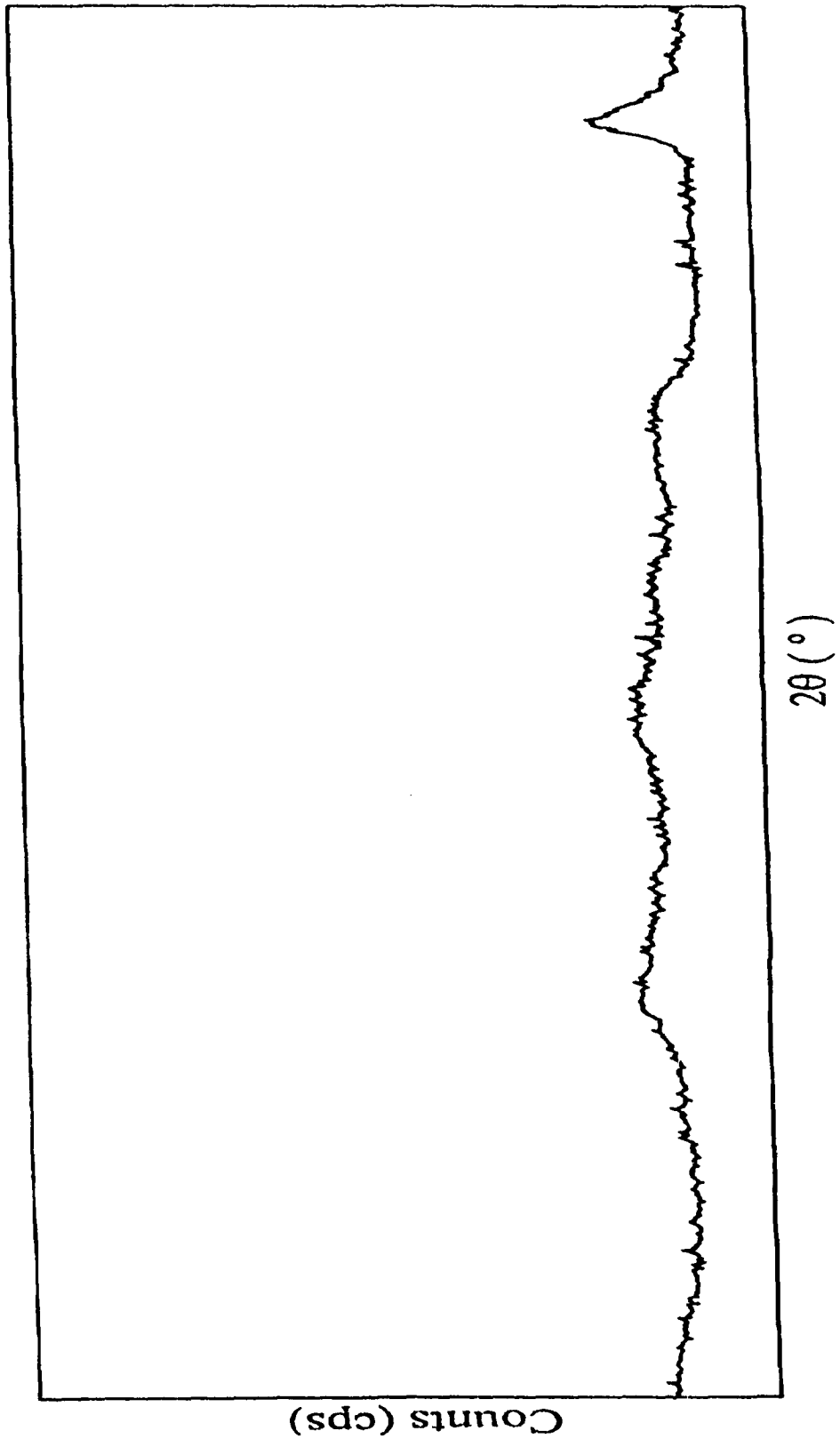


Fig. 2.3. Powder X-ray diffraction pattern of polypyrrole Th(IV) phosphate (as prepared).

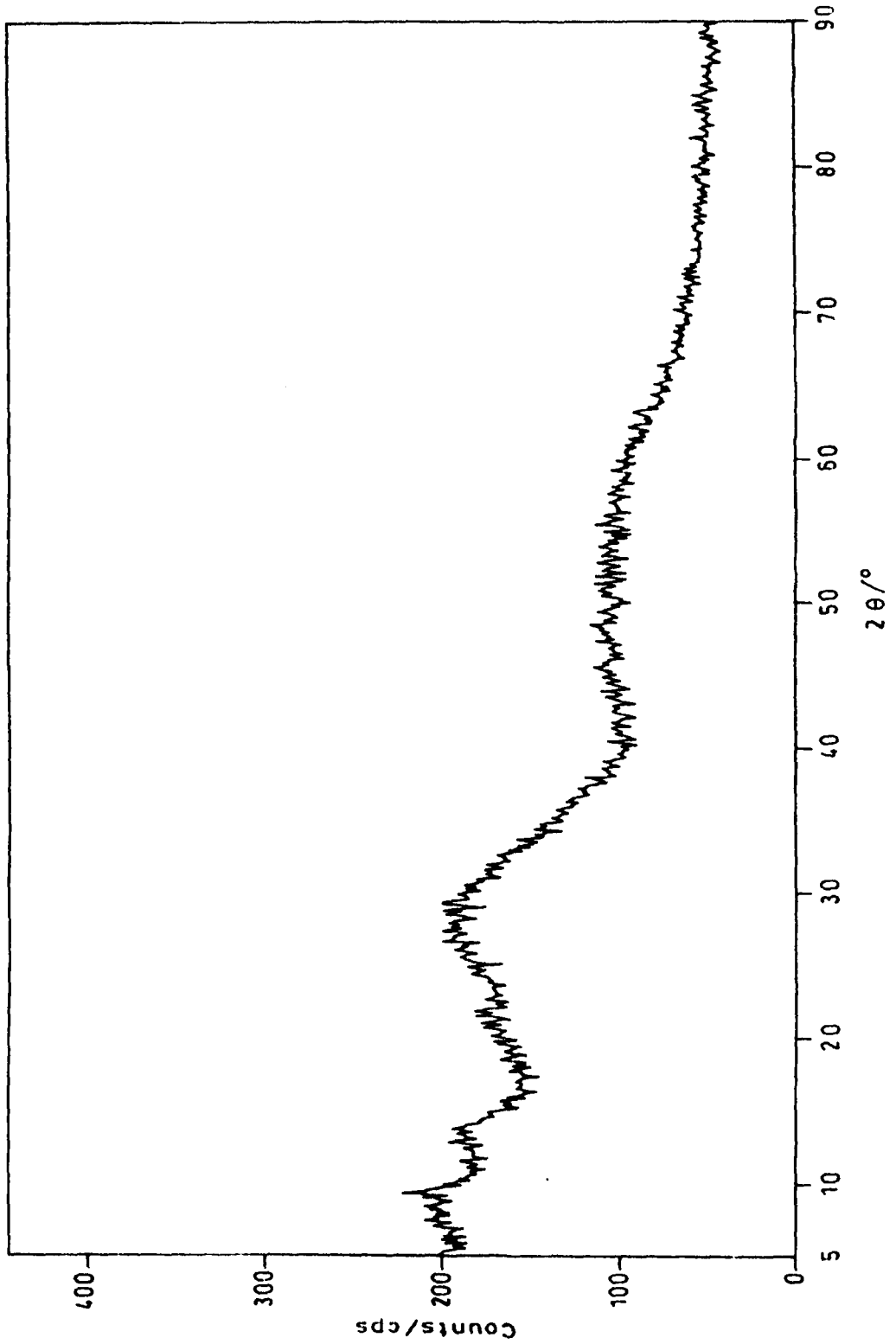


Fig. 2.4. Powder X-ray diffraction pattern of polyaniline Sn(IV) phosphate (as prepared).

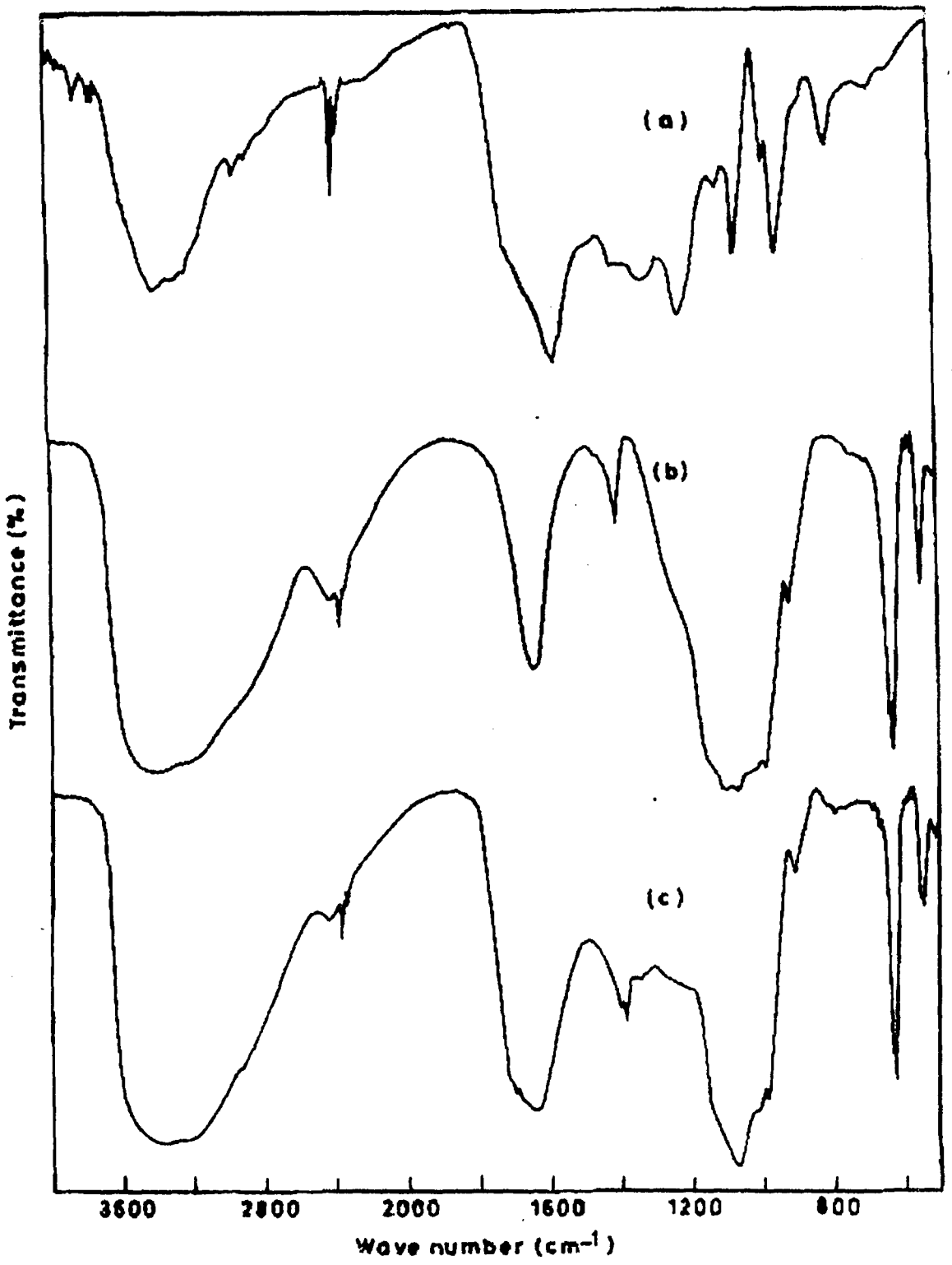


Fig. 2.5. FTIR spectra of as prepared polypyrrole (a), Th(IV) phosphate (b) and polypyrrole Th(IV) phosphate composite material (c).

Table 2.7

FTIR peaks positions (cm^{-1}) of polypyrrole (S-7), Th(IV) phosphate (S-6) and polypyrrole Th(IV) phosphate (S-5) composite cation-exchanger

Peaks no.	Polypyrrole (as prepared, dried at 50°C)	Thorium(IV) phosphate (as prepared, dried at 50°C)	Polypyrrole Th(IV) phosphate (as prepared, dried at 50°C)
1	667	546	510
2	792	572	551
3	932	624	576
4	968	631	626
5	1050	915	668
6	1100	976	796
7	1210	1063	910
8	1312	1097	984
9	1398	1400	1080
10	1560	1636	1339
11	2333	2364	1386
12	2364	2421	1400
13	2922	3417	1647
14	3389		2334
15	3736		2365
16	3822		2426
17			3397
18			3400

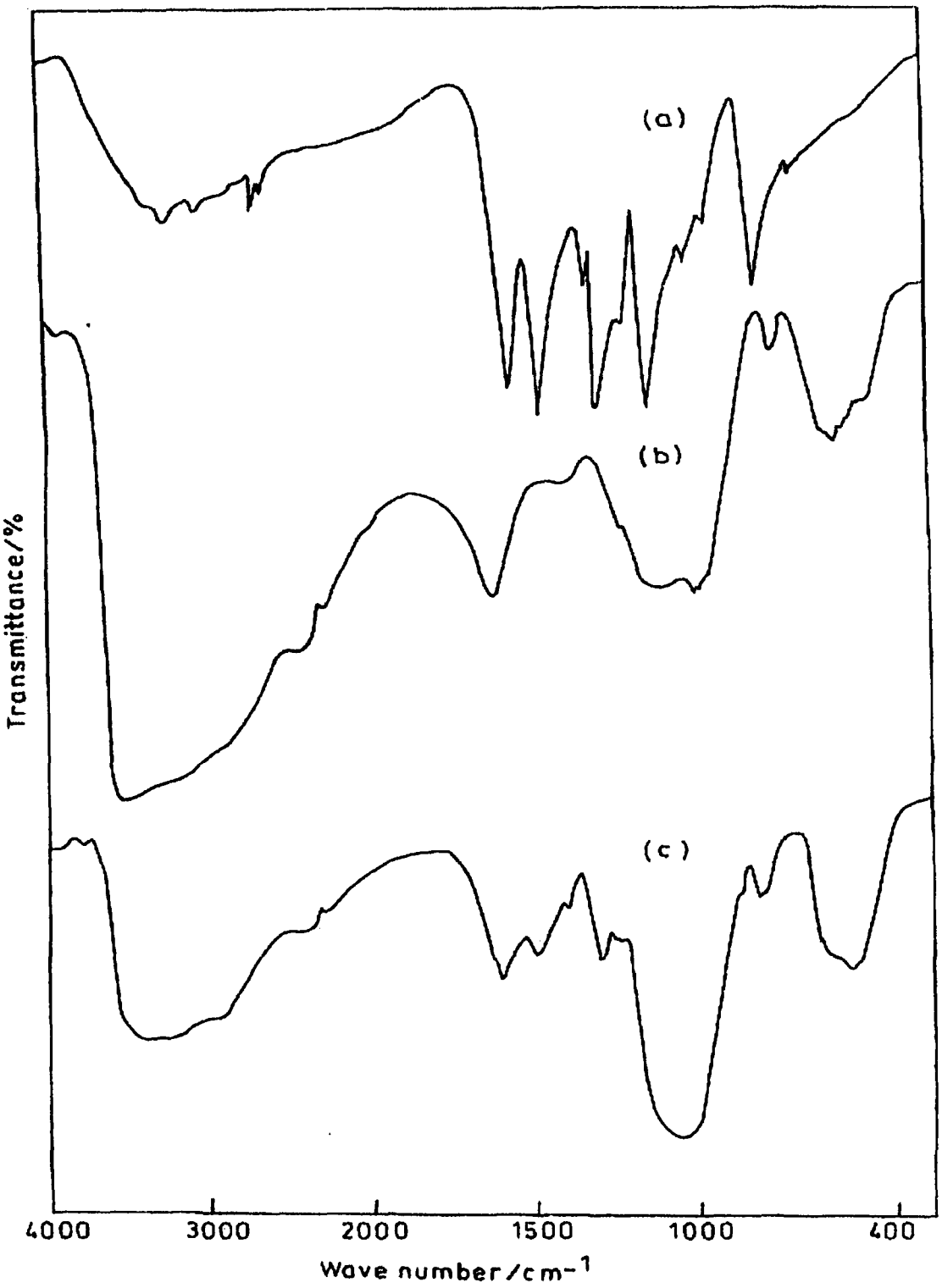


Fig. 2.6. FTIR spectra of as prepared polyaniline (a), Sn(IV) phosphate (b) and polyaniline Sn(IV) phosphate composite material (c).

Table 2.8

FTIR peaks positions (cm^{-1}) of polyaniline (T-5), Sn(IV) phosphate (T-6) and polyaniline Sn(IV) phosphate (T-7) composite cation-exchanger

Peaks no.	Polyaniline (as prepared, dried at 50°C)	Sn(IV) phosphate (as prepared, dried at 50°C)	Polyanline Sn(IV) phosphate (as prepared, dried at 50°C)
1	3035	3345	3400
2.	2846	2447	1611
3.	2358	1634	1493
4.	1587	1423	1300
5	1497	1136	1044
6	1371	1010	810
7	1302	586	540
8	1241		
9	1143		
10	1008		
11	954		
12	824		
13	728		

'organic-inorganic' composite cation-exchanger in H^+-form sample T-7 (Fig. 2.6 (c)) that the material shows the presence of external water molecule in addition to – OH groups and the metal oxygen bond. In the spectrum of the material a strong and broad band around 3400 cm^{-1} is found which can be ascribed to – OH stretching frequency. A sharp peak around 1600 cm^{-1} can be attributed to H-O-H bending band, which represents the strongly bonded – OH groups in the matrix [71]. The – OH stretching bands merge together and shifted to lower frequency in the spectrum of the composite cation-exchanger. A strong and broad band around 1000 cm^{-1} may represent the presence of ionic phosphate groups [72]. An assembly of two sharp peaks in the region 500-800 cm^{-1} may be due to the presence of metal oxygen bond [74,75].

In the sample of Sn(IV) phosphate (Fig. 2.6 (b)), there is a very strong and very broad – OH stretching band around 3500 cm^{-1} region and two very strong band around 800 cm^{-1} and 1000 cm^{-1} region are due to the presence of Sn-O stretching frequency and ionic phosphate groups, respectively. These characteristic stretching frequencies show close resemblance with the inorganic precipitate *i.e.* tin(IV) phosphate (Fig. 2.6 (b)) and polyaniline Sn(IV) phosphate (Fig. 2.6 (c)), indicating the binding of inorganic precipitate with organic polymer and formation of 'organic-inorganic' composite 'polyaniline Sn(IV) phosphate'. Another assembly of two peaks in the region 1300-1400 cm^{-1} may be ascribed due to the stretching vibration frequency of C-N [75] in the material (Fig. 2.6 (c)), as it is also resemble with the stretching vibration frequencies for C-N found in polyaniline (Fig. 2.6 (a)). This indicates that the polyaniline Sn(IV) phosphate contains considerable amount of aniline.

2.3.7. Thermogravimetric analyses-differential thermal analyses (TGA-DTA) studies

The thermogravimetric analyses (TGA-DTA) curve of composite cation-exchanger polypyrrole Th(IV) phosphate sample S-5 (Fig. 2.7) showed continuous weight loss of mass (about 12%) upto 174 °C, which may be due to removal of external water molecule [76]. Slow weight loss observed between 174 °C and 319 °C (may be due to the condensation of phosphate groups) to pyrophosphate groups. Further weight loss between 319 °C and 645 °C may be due to complete decomposition of the organic part of the material. At 645 °C onwards, a smooth horizontal section which represents the complete formation of the oxide form of the material. These transformations have also been supported by differential thermal analysis (DTA). The DTA curve indicates two exothermic peaks with maxima at 326 °C and 497 °C that also confirm the structural transformation in the material. The weight loss percent with increasing temperatures observed by TGA curve for polypyrrole Th(IV) phosphate composite cation-exchanger also supported by the thermal stability experiment Table 2.5

The TGA-DTA analyses curve (Fig. 2.8) of the polyaniline Sn(IV) phosphate sample T-7 showed continuous weight loss of mass (about 12.42%) upto 135 °C, which may be due to the removal of external water molecule [76]. A slow weight loss (~ 9.02%) observed between 135 and 398 °C (may be due to the condensation of phosphate groups) to pyrophosphate groups. Further weight loss (~ 12.03%) between 398 and 601 °C may be due to the complete decomposition of the organic part of the

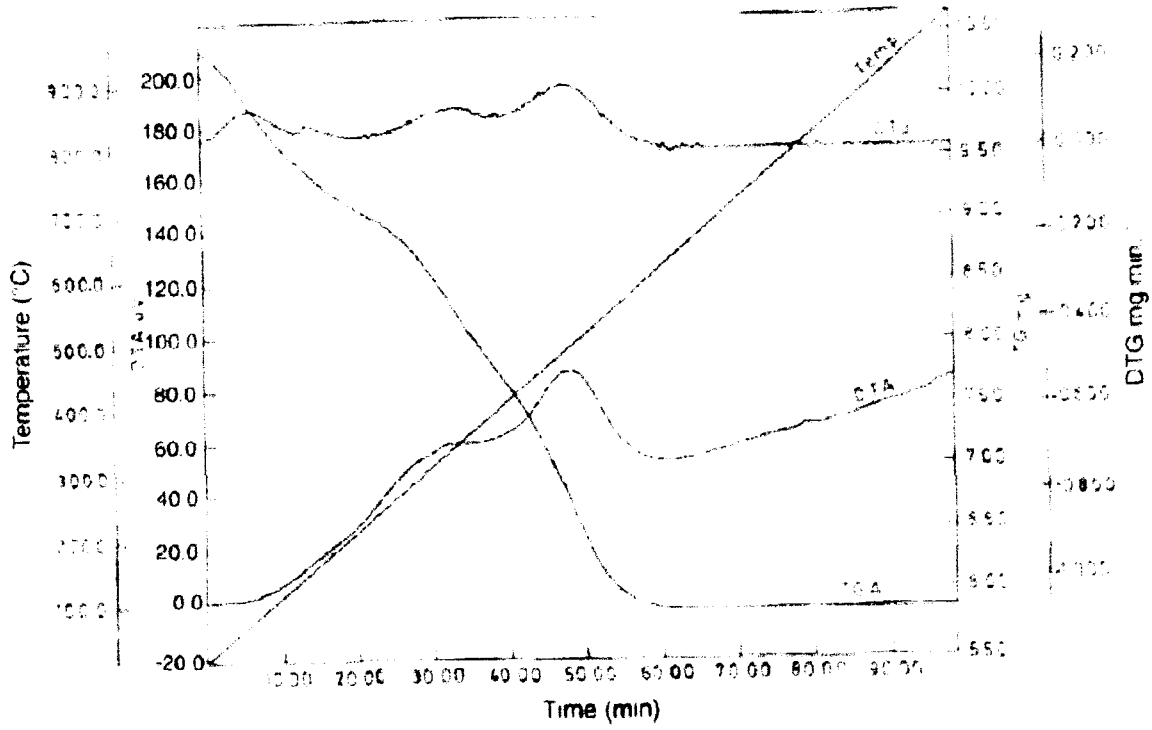


Fig. 2.7. Simultaneous TGA-DTA curves of polypyrrole Th(IV) phosphate (as prepared).

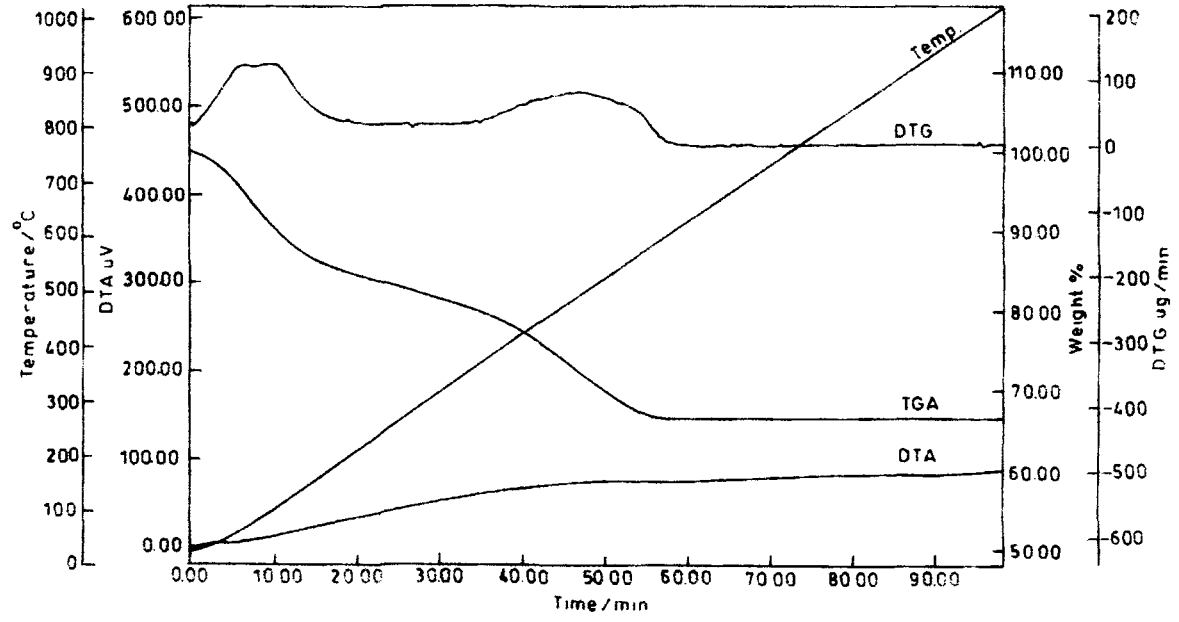


Fig. 2.8. Simultaneous TGA-DTA curves of polyaniline Sn(IV) phosphate (as-prepared).

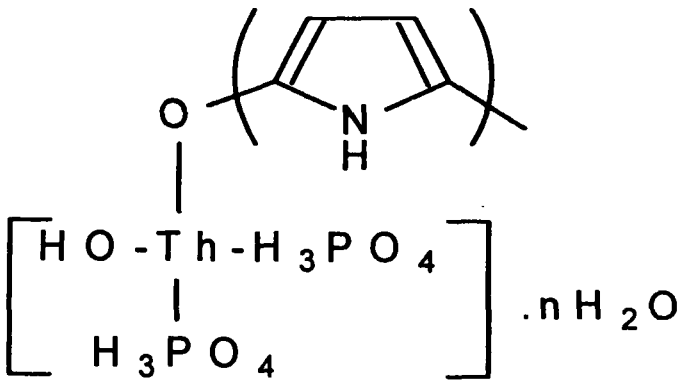
material. At 601 °C onwards, a smooth horizontal section represents the complete formation of the oxide form of the material. The weight loss percent with increasing temperatures observed by TGA curve for polyaniline Sn(IV) phosphate is also supported by the thermal stability experiment Table 2.5.

2.3.8. Chemical composition studies and chemical structure

The molar ratio of Th, P, C, H, N, and O in the composite cation-exchanger polypyrrole Th(IV) phosphate (sample S-5, as prepared) was estimated to be 1:2.34:11.77:25.36:2.73:15.21, which can suggest the following formula of the material:

$[(ThO_2)\ (H_3PO_4)_2.(-C_4H_2NH-)_3]\ .nH_2O$

and its structure can be written as:



Assuming that only the external water molecules are lost at 174 °C and ~12% weight loss of mass represented by TGA curve for sample S-5 must be due to the loss of nH_2O from the above structure. The value of '*n*' the external water molecules can be calculated using Alberti's equation [77]:

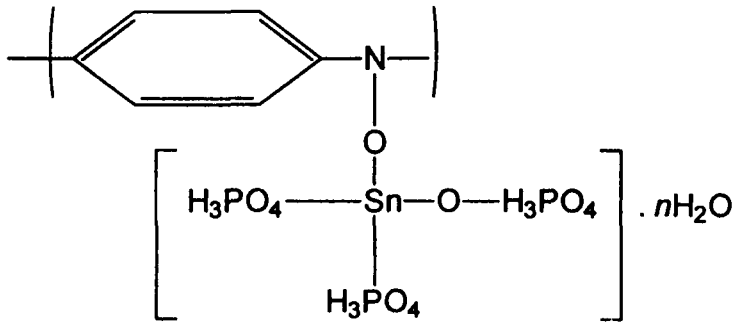
$18n = X(M+18n)/100$

Where X is the percent weight loss (~12%) the exchanger by heating upto 174 °C and (M+18n) is the molecular weight of the material. The calculations give ~5 for the external water molecule (n) per molecule of the cation-exchanger (sample S-5).

The molar ratio of Sn, P, C, II, N, and O in the composite cation-exchanger polyaniline Sn(IV) phosphate was also estimated as 1:3.28:6:24.50:1.07:23.57, which can suggest the following formula of the material:

$[(SnO_2)\ (H_3PO_4)_3.(-C_6H_4NH-)]\ .nH_2O$

and its structure can be written as:



Assuming that only the external water molecules are lost at 135 °C and ~12.42% weight loss of mass represented by TGA curve must be due to the loss of $n$$H_2O$ from the above structure. The value of 'n' the external water molecules can be calculated using Alberti's equation. The calculations give ~ 5 for the external water molecule (n) per molecule of the cation-exchanger (sample S-7).

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Chapter 3

Studies on Ion-Exchange Properties of Polypyrrole Th(IV) Phosphate & Polyaniline Sn(IV) phosphate Composite Cation-Exchangers

Chapter 3

3.1. Introduction

In recent years, synthetic inorganic ion-exchangers have established [1-3] their place in analytical chemistry due to their resistant to heat and radiation, their differential selectivity for metal ions. A large number of such materials have been synthesized earlier, most of which are the hydrous oxides and the heteropolyacids salts of the tetra and pentavalent metals. These compounds have shown great promise in analytical chemistry because of their separation potential of metals [4]. Every synthetic inorganic ion-exchanger has specific selectivity towards one or two metallic species. They are also highly stable to a wide range of pH and upto high temperature. However, their real analytical applications in various fields are still lacking.

Two component inorganic ion-exchangers have much studied as compared to three component ion-exchangers. The compound containing two different cations and one anion or two different anions and one cation (*i.e.* three component ion-exchangers) show specific selectivity and higher thermal stability. A number of two component [5,6], and three component [7,8] ion-exchangers have been established for the selective determination of heavy toxic metal ions. Since organic polymers as ion-exchangers are well known for their uniformity, chemical stability and control of their ion-exchange properties through synthetic methods [9-11]. Derivatization of inorganic ion-exchangers by organic molecules depends on the nature of the inorganic matrix. Tetravalent metal acid salts can be derivatized by organic moieties

bearing inorganic groups such as -OH, -COOH, $-SO_3H$, $-NH_2$, >NH *etc.* which also act as ion-exchangers, and are known as 'organic-inorganic' ion-exchangers or as derivatized tetravalent metal acid (DTMA) salts [12-22].

To obtained novel properties by the combination of organic and inorganic materials as ion exchangers, efforts have been made to develop ion exchangers by the incorporation of multivalent metal acid salts and organic conducting polymers (polyaniline, polypyrrole and polythiophene *etc.*), providing a new class of 'organic-inorganic' composite ion exchangers with better mechanical and granulometric properties, good ion exchange capacity, higher chemical, thermal and mechanical stabilities, reproducibility and possessing good selectivity for heavy metals indicating its useful environmental applications. Few such excellent ion exchange materials have been developed in our laboratory and successfully being used in environmental analysis [23-38].

Many studies on the ion-exchange kinetics of metal ions on organic and inorganic ion-exchangers have been reported [27,39-43]. However very few such information is available for the exchange on electrically conducting organic-inorganic composite cation-exchangers. These studies enable us to understand the viability of an ion-exchanger in separation of metal ions. Thus, to understand the theoretical aspects of ion-exchange separations it is very essential to study the kinetics of this process. In view of aforesaid facts, investigations of some kinetic parameters such as the diffusion coefficient, energy and entropy of activation, etc., are very much essential. It is noteworthy that these parameters tell us about the

mechanism, rate determining step and rate laws obeyed by the ion-exchange process. Moreover, the earlier approaches [44-47] of kinetic behavior are based on the old *Bt* criterion [48,49], which is not very useful for a true ion-exchange (non-isotopic exchange) process because of the different effective diffusion coefficients and different mobilities [50] of the exchanging ions involved. The Nernst-Planck [51,52] equations with some additional assumptions provide more appropriate values in obtaining the values of the various kinetic parameters precisely [30,31,53-57].

Since these electrically conducting composite polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate have possessed good ion-exchange behavior [24,37], we have also conducted a kinetic study on the exchange of some divalent metal ions on these materials [33,34], that is useful to understand the mechanism of ion-exchange on the surface of these materials and its separation potential. In this chapter, the studies of ion-exchange properties on these electrically conducting composite cation-exchange materials are described.

3.2. Experimental

3.2.1. Reagents and chemicals

The main reagents used for the synthesis were: Thorium nitrate ($Th(NO_3)_4.5H_2O$, 99%, CDH India Ltd.), Stannic chloride ($SnCl_4.5H_2O$, 97.5%, CDH India Ltd.), Phosphoric acid (H_3PO_4, 88-93%, Loba Chemie India Ltd.), Di-sodium hydrogen orthophosphate (Na_2HPO_4, CDH India Ltd.), Pyrrole (C_4H_4NH, 98%, E-Merck India Ltd.), Aniline ($C_6H_5NH_2$, 99%, Qualigens India Ltd.), Toluene ($C_6H_5CH_3$, 95%, CDH India Ltd.), Ferric chloride ($FeCl_3$, 96%, CDH India Ltd.), Potassium persulphate ($K_2S_2O_8$, 98%, CDH India Ltd.) Hydrochloric acid (HCl, 35%) and Nitric acid (HNO_3), 35%, E-Merck India Ltd. All other reagents and chemicals were of analytical reagent grade.

3.2.2. Instrumentation

- A water bath incubator shaker having a temperature variation of ± 0.5 °C was used for all equilibrium studies.
- An electronic balance (digital) - Sartorius (Japan), model 21 OS was used for weighing purpose.

3.2.3. Preparation of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers

Various samples of 'polypyrrole Th(IV) phosphate' and 'polyaniline Sn(IV) phosphate' were prepared by following the method as given in Chapter – 2 (Section 2.2.3.). On the basis of Na^+ ion-exchange capacity and reproducibility, the samples S-

5 (Table 3.1) and sample T-7 (Table 3.2) were chosen from both the composites for the detail studies of their ion-exchange behavior.

3.2.4. Ion-exchange properties of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate

3.2.4.1. Ion-exchange capacity (I.E.C.)

Polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate are cation-exchangers. The exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation-exchangers was determined by standard column process. For this purpose, one gram (1g) of the both dry cation-exchangers, sample S-5 and sample T-7 in the H^+-form were taken into two different glass columns having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1 M alkali and alkaline earth metal nitrates as eluents were used to elute the H^+ ions completely from the cation-exchange columns, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluents were titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solutions using phenolphthalein indicator and the ion-exchange capacities (I.E.C.) in meq g^{-1} are given in Table 3.3.

3.2.4.2. Effect of eluent concentration

To find out the optimum concentration of the eluent for complete elution of H^+ ions, a fixed volume (250 ml) of sodium nitrate ($NaNO_3$) solution of varying concentrations were passed through the columns of both cation-exchangers

Table 3.1

Preparation and ion-exchange capacity of various samples of polypyrrole Th(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratios (v/v)					Na^+ ion-exchange capacity (meq dry g^{-1})
	0.1 M $Th(NO_3)_4.5H_2O$ in 1 M HNO_3	H_3PO_4	Digestion time (h)	0.1 M $FeCl_3$	Pyrrole in toluene (33.33%)	
S-1	5	2 (1 M)	4	2	0.30	1.19
S-2	5	2 (1 M)	24	2	0.30	0.78
S-3	5	3 (1 M)	4.30	2	0.30	1.10
S-4	5	2 (2 M)	24	2	0.30	0.62
S-5	5	2 (2 M)	5	2	0.30	1.56
S-6	5	2 (2 M)	5	-	-	0.72
S-7	-	-	-	2	0.30	0.05
S-8	5	2 (2 M)	5	2	0.18	0.58
S-9	5	2 (2 M)	5	2.5	0.42	0.27
S-10	5	2 (2 M)	5	2.5	0.60	0.29
S-11	5	2 (2 M)	5	2.5	0.75	0.51
S-12	5	2 (2 M)	5	2.5	0.90	0.31

Table 3.2

Preparation and ion-exchange capacity of various samples of polyaniline Sn(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratios (v/v)					Na^+ ion -exchange capacity (meq dry g^{-1})
	0.1 M $SnCl_4.5H_2O$ in 4 M HCl	0.1 M Na_2HPO_4 in DMW	pH of the inorganic precipitate	0.1 M $K_2S_2O_8$ in 1 M HCl	10% Aniline in 1 M HCl	
T-1	1	1	1.0	1	1	1.10
T-2	1	2	1.0	1	1	1.45
T-3	2	1	1.0	1	1	0.85
T-4	2	2	1.0	1	1	0.96
T-5	-	-	-	1	1	0.20
T-6	2	3	1.0	-	-	1.12
T-7	2	3	1.0	1	1	1.96
T-8	1	3	1.0	1	1	0.58
T-9	1	4	1.0	1	1	0.45
T-10	3	4	1.0	1	1	0.72
T-11	2	3	1.0	2	1	1.20
T-12	2	3	1.0	1	2	0.98
T-13	2	3	1.0	2	2	1.40
T-14	2	3	1.0	3	2	0.92
T-15	2	3	1.0	2	3	0.85

Table 3.3

Ion-exchange capacity of various exchanging ions on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers

Exchanging ions	pH of the metal solutions	Ionic radii (A°)	Hydrated ionic radii (A°)	Ion-exchange capacity (meq dry g^{-1})			
				Polypyrrole Th(IV) phosphate (S-5)		Polyaniline Sn(IV) phosphate (T-7)	
				H^+ -liberation	H^+ -absorption	H^+ -liberation	H^+ -absorption
Li^+	6.7	0.68	3.40	1.05	1.00	1.43	1.41
Na^+	6.7	0.97	2.76	1.56	1.29	1.96	1.82
K^+	6.8	1.33	2.32	1.21	1.22	2.07	2.09
Mg^{2+}	6.5	0.78	7.00	1.15	1.17	2.05	2.03
Ca^{2+}	6.5	1.06	6.30	1.38	1.35	2.15	2.16
Sr^{2+}	6.3	1.27	-	1.89	1.85	2.26	2.29
Ba^{2+}	6.3	1.43	5.90	2.74	2.75	2.32	2.33

containing 1 g of the exchanger each, in the H^+-form with a flow rate of ~0.5 ml min^{-1}. The effluents were titrated against a standard alkali solution of 0.1 M NaOH for the H^+ ions eluted out. Table 3.4 showed the maximum elution observed with the concentration of $NaNO_3$ for both the composite cation-exchangers.

3.2.4.3. Elution behavior

Since an optimum concentration for a complete elution for both the composite cation-exchangers sample polypyrrole Th(IV) phosphate S-5 and sample polyaniline Sn(IV) phosphate T-7 was observed to be 1 M (Table 3.4), two different columns containing 1 g of the each exchanger in H^+- form were eluted with $NaNO_3$ solution of this concentration in different 10 ml fractions with minimum flow rate as described above and each fractions of 10 ml effluent was titrated against a standard alkali solution for the H^+ ions eluted out. This experiment was conducted to find out the minimum volume necessary for almost complete elution of H^+ ions which determines the exchange efficiency of the column.

3.2.4.4. pH – titration

pH-titration studies of polypyrrole Th(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7) were performed by the method of Topp and Pepper [58]. A total of 500 mg portions of both the cation-exchangers in the H^+-form were placed in each of the several 250 ml conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratio, the final volume being 50 ml to maintain the ionic strength constant. The pH of the

Table 3.4

Effect of eluent concentration on ion-exchange capacity of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers

S. No.	Polypyrrole Th(IV) phosphate (S-5)		Polyaniline Sn(IV) phosphate (T-7)	
	Molar concentration of $NaNO_3$	Ion-exchange capacity (meq dry g^{-1})	Molar concentration of $NaNO_3$	Ion-exchange capacity (meq dry g^{-1})
1	0.25 M	0.60	0.2 M	0.85
2	0.50 M	0.83	0.4 M	1.20
3	0.75 M	1.05	0.6 M	1.40
4	1.00 M	1.56	0.8 M	1.75
5	1.50 M	1.56	1.0 M	1.96
6	2.00 M	1.56	1.2 M	1.96
7	3.00 M	1.56	1.4 M	1.96
9	-	-	1.6 M	1.96

solution was recorded [59-61] after every 24 h until equilibrium was attained, which needed ~5 days and pH at equilibrium was plotted against the milliequivalents of OH^- ions added.

3.2.4.5. Thermal effect on ion-exchange capacity (I.E.C.)

To study the effect of drying temperature on the i.e.c., 1 g samples of both the composite cation-exchange materials (S-5) and (T-7) in the H^+-form were heated at various temperatures in a muffle furnace for 1 hour each and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature. The results are given in Table 3.5.

3.2.4.6. Selectivity (sorption) studies

The distribution behavior of metal ions plays an important role in the determination of selectivity of the material. In certain practical applications, equilibrium is most conveniently expressed in terms of distribution coefficients of the counter ions.

The distribution coefficient (K_d values) of various metal ions on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate were determined by batch method in various solvents systems. Various 200 mg of the composite cation-exchangers beads sample S-5 and sample T-7 in the H^+-form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and kept for 24 hours with continuous shaking for 6 hours in a temperature controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion

Table 3.5

Effect of temperature on ion-exchange capacity (i.e.c.) of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers on heating time for one hour

S. No.	Heating temperature (°C)	Polypyrrole Th(IV) phosphate (S-5)		Polyaniline Sn(IV) phosphate (T-7)	
		Na^+ ion-exchange capacity (meq dry g^{-1})	% Retention of i.e.c.	Na^+ ion-exchange capacity (meq dry g^{-1})	% Retention of i.e.c.
1	40	1.56	100	1.96	100
2	100	1.56	100	1.96	100
3	150	1.56	100	1.96	100
4	200	1.32	84.61	1.71	87.12
5	300	0.96	61.54	1.42	72.46
6	350	0.87	55.77	1.16	59.31
7	400	0.45	28.85	0.77	39.29
8	500	0.33	21.15	0.53	26.94
9	600	0.22	14.10	0.22	11.02

concentration was to adjust that it did not exceed 3% of its total ion exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solution of EDTA [62]. The alkali and alkaline earth metal ions [K^{+}, Na^{+}, Ca^{2+}] were determined by flame photometry and some heavy metal ions such as [Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution quantity is given by the ratio of amount of metal ion in the exchanger phase and in the solution phase. In other word, the distribution coefficient is the measure of a fractional uptake of metal ions competing for H^{+} ions from a solution by an ion-exchange material and hence mathematically can be calculated using the formula given as:

$$K_d = \frac{\text{m moles of metal ions / gm of ion-exchanger}}{\text{m moles of metal ions / ml of solution}} \ (\text{ml g}^{-1}) \qquad \ldots\ldots 3.1$$

$$i.e. \quad K_d = [(I-F)/F] \times V/M \ (ml\, g^{-1}) \qquad \ldots\ldots 3.2$$

where I is the initial amount of metal ion in the aqueous phase, F is the final amount of metal ion in the aqueous phase, V is the volume of the solution (ml) and M is the amount of cation-exchanger (g).

3.2.4.7. Separation factors

The separation factor may be considered as the relative tendency of two ions to be adsorbed in an exchanger from solutions of equal concentration. It is used as a measure of possibility of chromatographic separation and is also expressed as the ratio of the distribution coefficients of the elements to be separated as:

$$Separation\ factor\ (\alpha_B^A) = \frac{K_d(A)}{K_d(B)} \quad \text{..... 3.3}$$

where K_d (A) and K_d (B) are the distribution coefficients for the two competing species A and B in the ion-exchange system. The separation factor is the preference of the ion-exchangers for one of the two counter ions is often. The quantity is particularly convenient for practical applications, *e.g.,* for the calculation of column preference.

3.2.4.8. Ion-exchange kinetics

The kinetic behavior of cation-exchange materials for the exchange of various metal ions were studied on both the composite cation-exchanger samples (S-5 and T-7) in the H^+- form.

3.2.4.8.1. Determination of the infinite time of exchange

The infinite time of exchange is the time necessary to obtain equilibrium in an ion-exchange process. The ion-exchange rate becomes independent of time after this time interval as evident from Fig. 3.1 and Fig. 3.2. About 20 minutes for sample S-5 and 25 minutes for sample T-7 were required for the establishment of equilibrium at 33 °C for Mg^{2+}-H^+ exchange. Similar behavior was observed for Ca^{2+}-H^+, Sr^{2+}-H^+, Ba^{2+}-H^+, Ni^{2+}-H^+, Cu^{2+}-H^+, Mn^{2+}-H^+ and Zn^{2+}-H^+ exchanges. Therefore, 25 and 20 minutes have been assumed to be the infinite time of exchange for these studies.

3.2.4.8.2. Kinetic measurements

The composite cation-exchange material samples (S-5 and T-7) were grounded

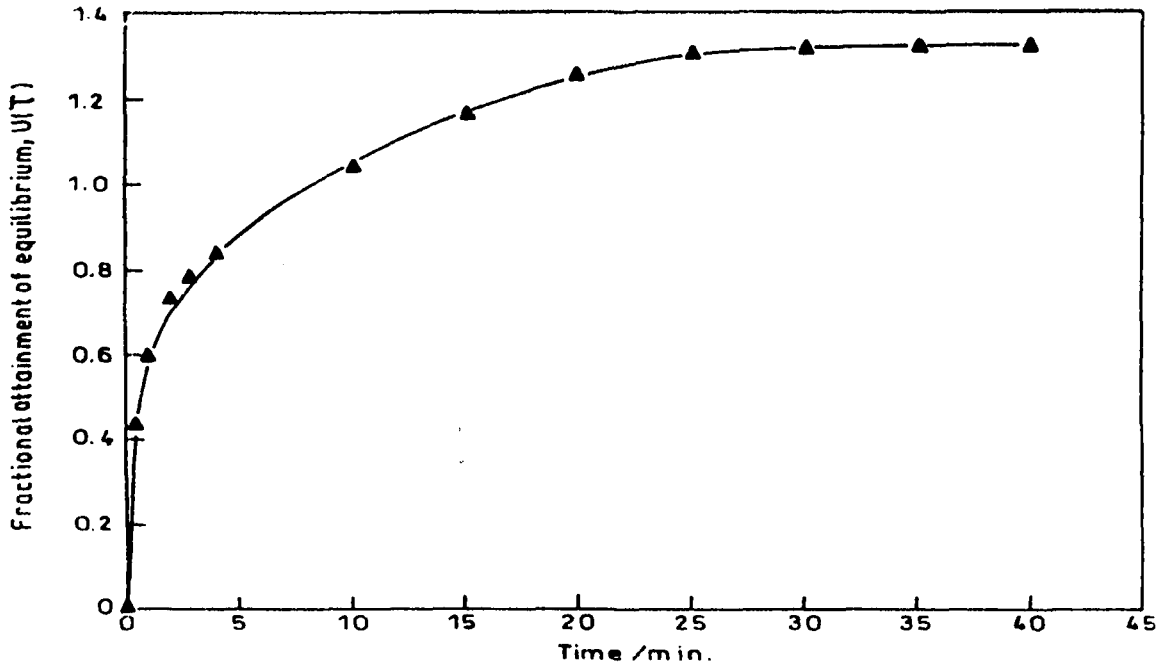

Fig. 3.1. A plot of U(τ) versus t (time) for M(II)-H(I) exchanges at 33°C on polypyrrole Th(IV) phosphate composite cation-exchanger for the determination of infinite time.

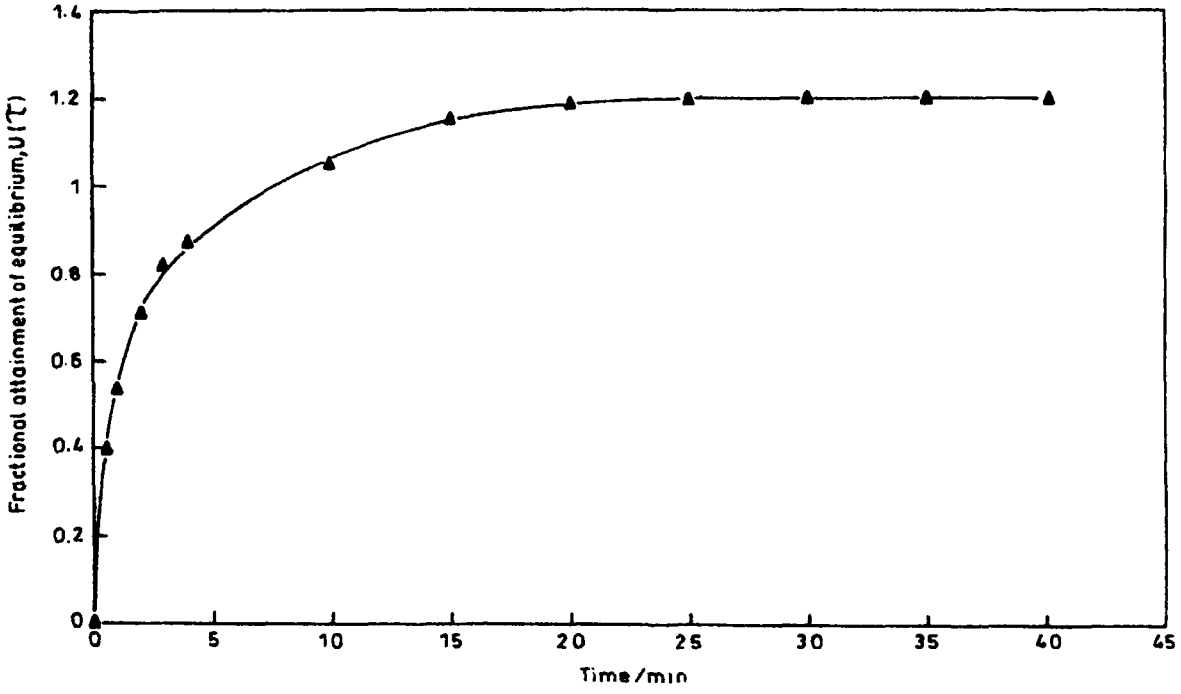

Fig. 3.2. A plot of U(τ) versus t (time) for M(II)-H(I) exchanges at 33°C on polyaniline Sn(IV) phosphate composite cation-exchanger for the determination of infinite time.

and then sieved to obtain particles of definite mesh sizes (25-50, 50-70, 70-100 and 100-125). Out of them the particles of mean radii ~125 μm (50-70 mesh) were selected to evaluate various kinetic parameters. The rate of exchange was determined by limited bath technique as follows:

Twenty-milliliter fractions of the 0.02 M metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn) were shaken with 200 mg of both the cation-exchangers in H^+-form in several stoppered conical flasks at desired temperatures (25, 33, 50 and 65 (±0.5) °C) for different time intervals (0.5, 1.0, 2.0, 3.0 and 4.0 min). The supernatant liquids were removed immediately and determinations were made usually by EDTA titrations [62]. Each set was repeated four times and the mean values were taken for calculations.

3.2.4.8.3. Analytical procedures

The results are expressed in terms of the fractional attainment of equilibrium $U(\tau)$ with time according to the equation:

$$U(\tau) = \frac{\textit{the amount of exchange at time 't'}}{\textit{the amount of exchange at infinite time}} \qquad \ldots\ldots 3.4$$

and the corresponding τ values were calculated by solving the Nernst-Plank equation [63,64]. The τ values for alkaline earth and transition metal ions on polypyrrole Th(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7) composite cation-exchangers are given in Table 3.6 at four different temperatures.

Table 3.6

τ-values for M^{2+}-H^{+} exchanges on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate cation-exchangers at different temperatures after various time intervals

Exchanging ions ⇓	τ - values at							
	Polypyrrole Th(IV) phosphate (S-5)				Polyaniline Sn(IV) phosphate (T-7)			
Temperature ⇒	25 °C	33 °C	50 °C	65 °C	25 °C	33 °C	50 °C	65 °C
Time (min.) ⇓								
Mg^{2+}-H^{+}								
0.5	0.028	0.033	0.042	0.058	0.032	0.04	0.05	0.068
1.0	0.059	0.068	0.084	0.112	0.066	0.076	0.095	0.120
2.0	0.125	0.147	0.171	0.210	0.134	0.157	0.188	0.224
3.0	0.199	0.226	0.263	0.315	0.209	0.24	0.276	0.335
4.0	0.260	0.294	0.351	0.426	0.272	0.31	0.363	0.444
Ca^{2+} - H^{+}								
0.5	0.030	0.037	0.047	0.055	0.034	0.042	0.053	0.061
1.0	0.062	0.076	0.089	0.104	0.066	0.082	0.095	0.110
2.0	0.128	0.148	0.168	0.187	0.132	0.153	0.177	0.204
3.0	0.193	0.216	0.241	0.264	0.202	0.227	0.258	0.303
4.0	0.262	0.290	0.317	0.347	0.270	0.301	0.336	0.403
Sr^{2+} - H^{+}								
0.5	0.014	0.023	0.032	0.042	0.017	0.026	0.036	0.048
1.0	0.035	0.049	0.049	0.080	0.040	0.054	0.069	0.092
2.0	0.080	0.104	0.104	0.155	0.092	0.113	0.135	0.173
3.0	0.128	0.158	0.158	0.230	0.136	0.170	0.203	0.255
4.0	0.172	0.211	0.211	0.301	0.185	0.225	0.272	0.342
Ba^{2+} - H^{+}								
0.5	0.019	0.030	0.038	0.049	0.027	0.034	0.042	0.060
1.0	0.041	0.058	0.074	0.093	0.050	0.066	0.082	0.110
2.0	0.093	0.124	0.150	0.182	0.107	0.135	0.171	0.221
3.0	0.143	0.183	0.223	0.267	0.163	0.200	0.255	0.321
4.0	0.189	0.242	0.298	0.355	0.210	0.265	0.350	0.428

Table 3.6 Continued

Exchanging ions ⇓	τ - values at							
	Polypyrrole Th(IV) phosphate (S-5)				Polyaniline Sn(IV) phosphate (T-7)			
Temperature ⇒	25 °C	33 °C	50 °C	65 °C	25 °C	33 °C	50 °C	65 °C
Time (min.) ⇓								
Mn^{2+}-H^{+}								
0.5	0.026	0.043	0.058	0.072	0.032	0.047	0.064	0.079
1.0	0.056	0.084	0.108	0.137	0.068	0.094	0.124	0.152
2.0	0.124	0.171	0.214	0.258	0.145	0.184	0.237	0.292
3.0	0.191	0.258	0.320	0.385	0.222	0.276	0.352	0.427
4.0	0.258	0.340	0.414	0.502	0.300	0.374	0.476	0.572
Zn^{2+} - H^{+}								
0.5	0.024	0.033	0.044	0.054	0.028	0.036	0.048	0.051
1.0	0.051	0.066	0.084	0.105	0.550	0.070	0.088	0.100
2.0	0.105	0.132	0.157	0.202	0.113	0.137	0.168	0.198
3.0	0.159	0.191	0.231	0.292	0.173	0.204	0.245	0.291
4.0	0.218	0.255	0.307	0.379	0.234	0.268	0.331	0.385
Cu^{2+} - H^{+}								
0.5	0.017	0.030	0.047	0.061	0.028	0.036	0.052	0.066
1.0	0.042	0.063	0.089	0.113	0.058	0.072	0.097	0.120
2.0	0.096	0.130	0.177	0.210	0.119	0.155	0.191	0.238
3.0	0.146	0.197	0.255	0.307	0.185	0.237	0.284	0.348
4.0	0.197	0.266	0.332	0.393	0.259	0.315	0.386	0.460
Ni^{2+} - H^{+}								
0.5	0.017	0.034	0.047	0.064	0.035	0.044	0.056	0.017
1.0	0.042	0.069	0.088	0.118	0.062	0.087	0.108	0.135
2.0	0.10	0.138	0.179	0.223	0.127	0.167	0.208	0.250
3.0	0.157	0.200	0.259	0.320	0.196	0.248	0.306	0.377
4.0	0.215	0.265	0.337	0.414	0.269	0.327	0.413	0.510

3.3. Results and Discussions

3.3.1. Preparation of organic-inorganic composite cation-exchangers and ion-exchange capacity (I.E.C.)

In this endeavor, various samples of new and novel 'organic-inorganic' composite cation-exchange materials were developed by incorporating electrically conducting polymers, polypyrrole and polyaniline into the inorganic matrices of fibrous Th(IV) phosphate and Sn(IV) phosphate, respectively. Due to the high percentage of yield, better ion-exchange capacity, reproducible behavior and chemical and thermal stabilities sample S-5 (Table 3.1) and sample T-7 (Table 3.2) were chosen for detail ion-exchange behavior studies. These composite cation-exchange materials possessed a better Na^+ ion-exchange capacity (1.56 meq g^{-1}) for polypyrrole Th(IV) phosphate as compared to inorganic precipitate of fibrous type Th(IV) phosphate (0.72 meq g^{-1}) and (1.96 meq g^{-1}) for polyaniline Sn(IV) phosphate as compared to Sn(IV) phosphate (1.12 meq g^{-1}) and also from some other similar materials prepared earlier (Table 3.7 and Table 3.8). However, these materials exhibited high granulometric and mechanical properties, showing a good reproducible behavior as is evident from the fact that these materials obtained from various batches did not show any appreciable deviation in their ion-exchange capacities.

The effect of the size and charge of the exchanging ions on the ion-exchange capacity was also observed for these materials. The ion-exchange capacity of these composite cation-exchangers for alkali metal ions and alkaline earth metal ions

Table 3.7

Comparison of the preparation and properties of polypyrrole Th(IV) phosphate with those of other cation-exchangers

Ion-exchange materials	Reagents	Mixing ratios	pH of the inorganic precipitates	Na^+-exchange capacity (meq dry g^{-1})
Polypyrrole Th(IV) phosphate (S-5)	0.1M Thorium nitrate in 1M nitric acid + 2 M H_3PO_4 + 0.1 M $FeCl_3$ + 33.33% pyrrole in toluene	5: 2: 2: 0.3	-	1.56
Thorium (IV) phosphate (S-6)	0.1M Thorium nitrate in 1M nitric acid +1M H_3PO_4	5: 2	-	0.72
Polypyrrole (S-7)	33.33% Pyrrole in CCl_4 + 0.1 M $FeCl_3$	1: 10	-	0.05
Polyacrylonitrile thorium(IV) phosphate	0.1M Thorium nitrate in 1M nitric acid +2 M $H_3P\ O_4$ + alcoholic solution of polyacrylonitrile	1:1	-	3.90
Thorium Iodate [65]	0.1M potassium iodate (in demineralized water) (DMW) + 0.1 thorium nitrate (in DMW)	1:1	1	1.23
Th(IV) antimonate [66]	0.1M thorium nitrate in 0.1M HNO_3 + 0.1M antimony(V) chloride in 4M HCl	1 : 1	-	2.00
Antimony(III) molybdate [67]	0.1M Sodium molybdate + 0.1M antimony(III) chloride	1 : 1	-	1.02
Antimony(III) arsenate [68]	0.05M Sodium arsenate + 0.05M antimony(III) chloride	1 : 1	0.85	0.70
Titanium(IV) arsenophosphate [69]	0.05 M Disodium hydrogen phosphate+ 0.05 M disodiumhydrogenarsenate + 0.05 M titanium (IV) chloride	1:1:1	4	2.80
Iron(III) tungstophosphate	0.1M $Fe(NO_3)_3$ + 0.1M sodium tungstate ($Na_2W\ O_4$) + 0.1M $(NH_4)H_2PO_4$	2:1:2	1	0.80
Ce(IV) silicate [70]	0.1 M Cerium(IV) sulfate + 0.1 M sodium silicate	1:3	9	1.2
Saw dust based Zr(IV) tungstophosphate [37]	Saw Dust gmL^{-1} + 0.1M Zirconium oxy chloride+ 0.1M sodium tungstate +0.1M orthophosphoric acid	2:1:1:3	-	1.52

Table 3.8

Comparison of the preparation and properties of polyaniline Sn(IV) phosphate with those of other cation-exchangers

Ion-exchange materials	Reagents	Mixing ratio	pH of the inorganic precipitates	Na^+-exchange capacity (meq dry g^{-1})
Polyaniline Sn(IV) phosphate (T-7)	0.1 M $SnCl_4.5H_2O$ in 4 M HCl + 0.1 M $K_2S_2O_8$ in 1 M HCl + 10 % Aniline in 1 M HCl + 0.1 M $K_2S_2O_8$	2:3:1:1	1	1.96
Tin(IV) phosphate (T-6)	0.1 M $SnCl_4.5H_2O$ in 4 M HCl + 0.1 M Na_2HPO_4 in DMW	2:3	1	1.12
Polyaniline (T-5)	0.1 M $K_2S_2O_8$ in 1 M HCl + 10 % Aniline in 1 M HCl	1:1	-	0.20
Polyaniline Sn(IV) tungstoarsenate [26]	0.1 M $SnCl_4.5H_2O$ + $Na_2HAsO_4.7H_2O$ + 0.1 M $Na_2WO_4.2H_2O$	1:1:1:1: 1	1	1.67
Cerium (IV) molybdate [71]	0.05 M Ceric ammonium nitrate + 0.1 M Ammonium molybdate	1:2	0.5	4.24
Tin(IV) tungstoselenate [72]	0.05 M $SnCl_4.5H_2O$ + 0.05 M Na_2SeO_3 + 0.05 M$Na_2WO_4.2H_2O$	1:2:1	-	1.07
Acrylamide Sn(IV) phosphate	0.3 M $SnCl_4.5H_2O$ + 0.6 M H_3PO_4 + Acrylamide	1:2:2	-	2.1
Sn(IV) tungstoarsenate [73]	0.25M Sn(IV) chloride + 0.25M sodium tungstate + 0.25 M sodium arsenate	2:1:1	1.0	1.06
Polyaniline Sn(IV) arsenophosphate [37]	0.1 M Sn(IV) chloride + 0.1 M sodium arsenate + 0.1 M H_3PO_4 + 10%aniline + 0.1 M $(NH_4)_2S_2O_8$	1:1:1:1: 1	1.0	1.58
Zirconium (IV) sulphosalicylophosphate [74]	0.05 M $ZrOCl_2.8H_2O$ + 0.05 M sulphosalicylic acid + 0.05 M H_3PO_4	2:1:2	2.5	1.72
Zirconium(IV) sulphosalicylate [75]	0.25 M $ZrOCl_2.8H_2O$ + sulphosalicylic acid	2:1	1.4	0.84
Zirconium(IV) 4-amino, 3 Hydroxy naphthalene sulfonate [76]	0.2 M $ZrOCl_2.8H_2O$ (A) + NH_4OH (B) + 4-amino, 3 hydroxy naphthalene sulfonate (C)	A:B-1:1.66 A:C-1:2	4~5	0.228

increased according to the decrease in their hydrated ionic radii as evident from Table 3.3. It was also found that the values of H^+-adsorption and H^+-liberation capacities are in close agreement.

The column elution experiments indicated a dependence of the concentration of the eluant on the rate of elution, which is a usual behavior for such materials. The minimum molar concentration of $NaNO_3$ as eluant for sample S-5 and sample T-7 was found 1 M for maximum release of H^+ ions from 1 g of the cation-exchanger as evident from Fig. 3.3 and Fig. 3.4. The elution behavior indicates that the exchange is quite fast at the beginning as all the exchangeable H^+ ions for both the ion-exchangers, i.e., polypyrrole Th(IV) phosphate sample (S-7) and polyaniline Sn(IV) phosphate sample (T-7) are eluted out in the first 150 ml of the effluent within 5 h as evident from Fig. 3.5 and Fig. 3.6.

3.3.2. pH - titration

The pH-titration curves for polypyrrole Th(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7) were obtained under equilibrium conditions with NaOH/NaCl, KOH/KCl and LiOH/LiCl. Both the systems indicated bifunctional behavior of the materials as shown in Fig. 3.7 and Fig. 3.8. The composite materials polypyrrole Th(IV) phosphate (S-5) and polyaniline (IV) phosphate (T-7) appear to be strong cation-exchangers as indicated by a low pH (~1.5) and pH (~2) of the solutions respectively, when no OH^- ions were added to the system. For the sample S-5, the rate of H^+-Na^+ exchange was faster than those of H^+-K^+ and H^+-Li^+ exchanges, while in case of sample T-7, the rate of exchange of H^+- K^+ exchange was

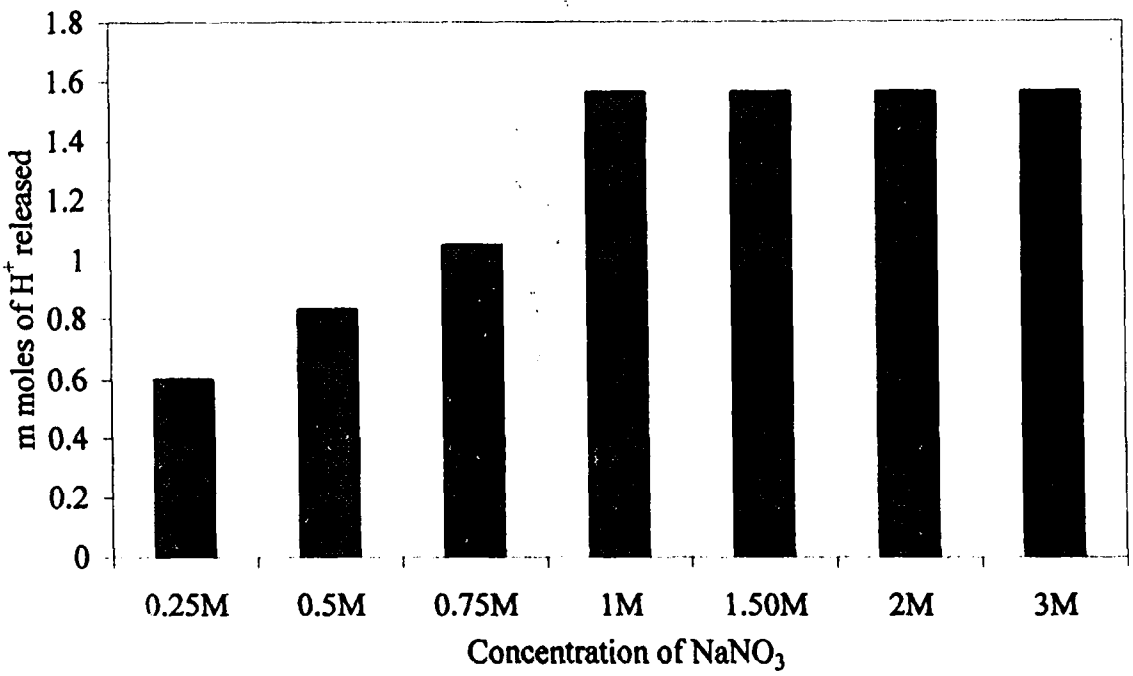

Fig. 3.3. Effect of eluent concentration on ion-exchange capacity of polypyrrole Th(IV) phosphate cation-exchanger.

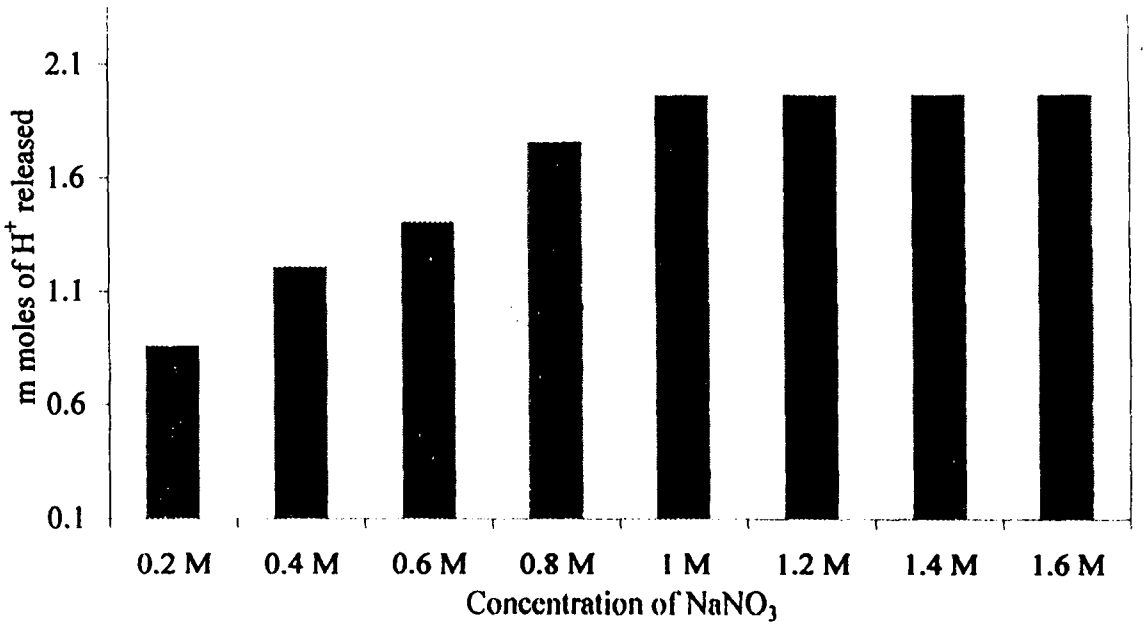

Fig. 3.4. Effect of eluent concentration on ion-exchange capacity of polyaniline Sn(IV) phosphate cation-exchanger.

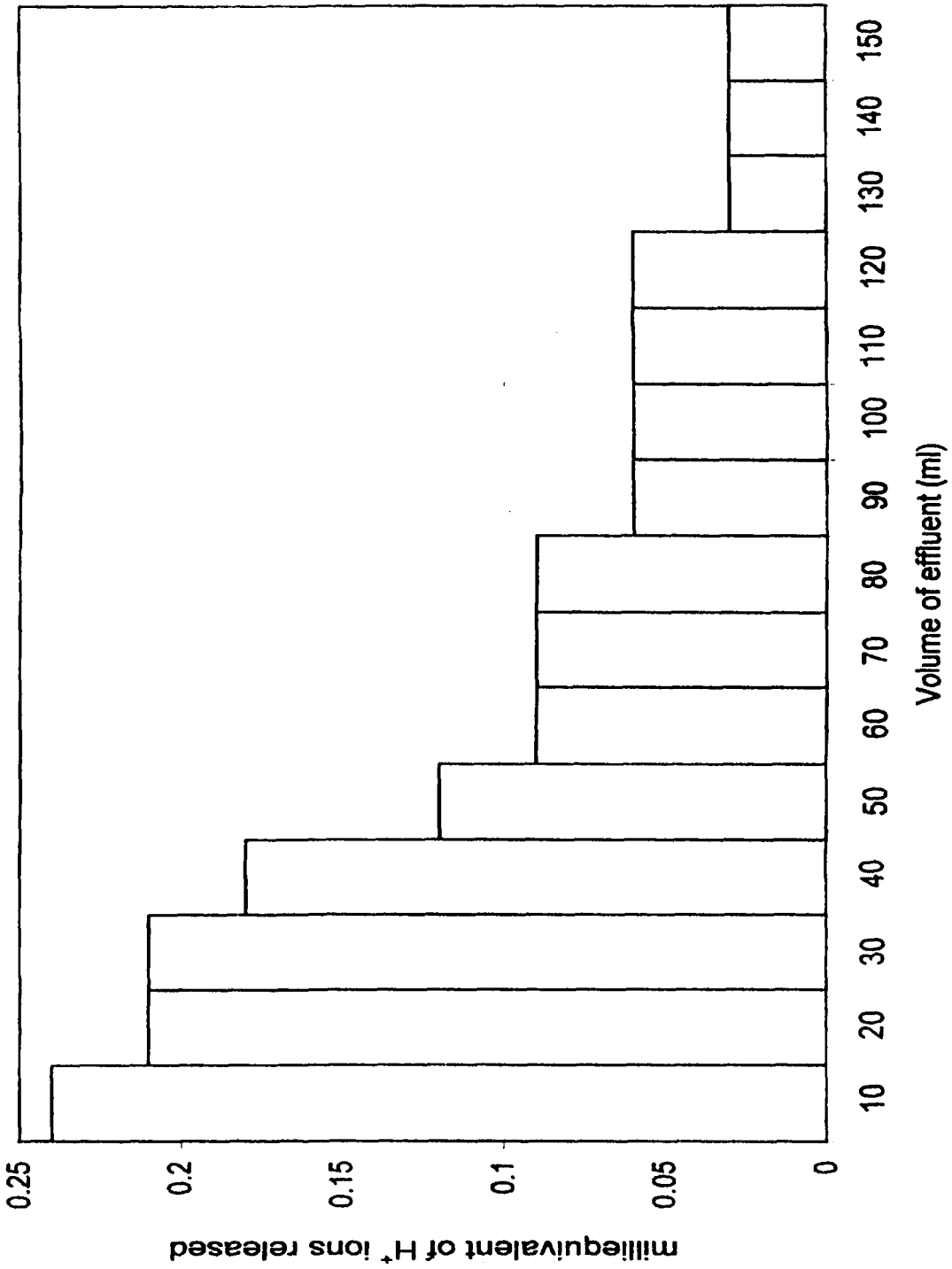

Fig. 3.5. Elution behavior of polypyrrole Th(IV) phosphate cation-exchange material.

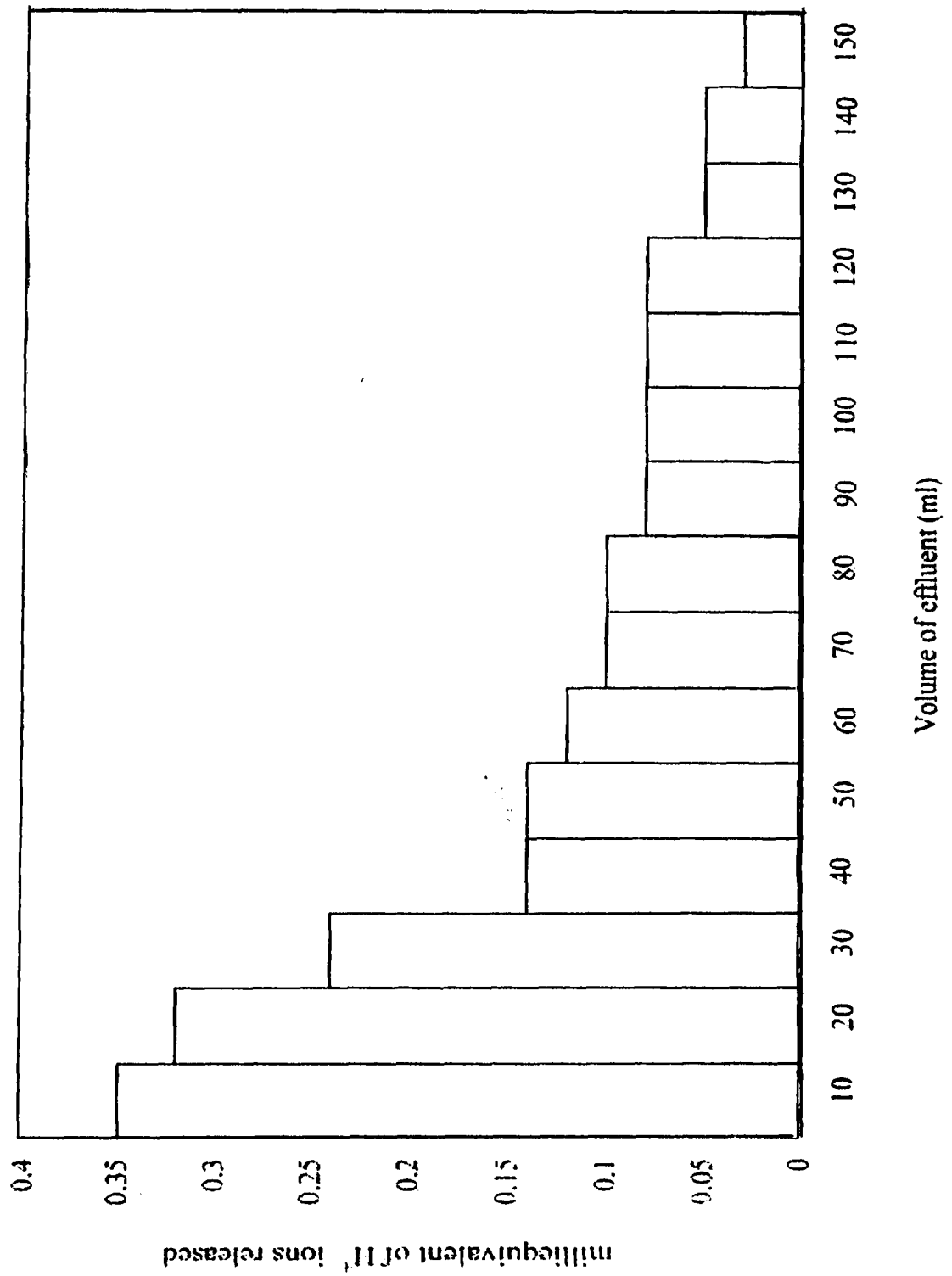

Fig. 3.6. Elution behavior of polyaniline Sn(IV) phosphate cation-exchange material.

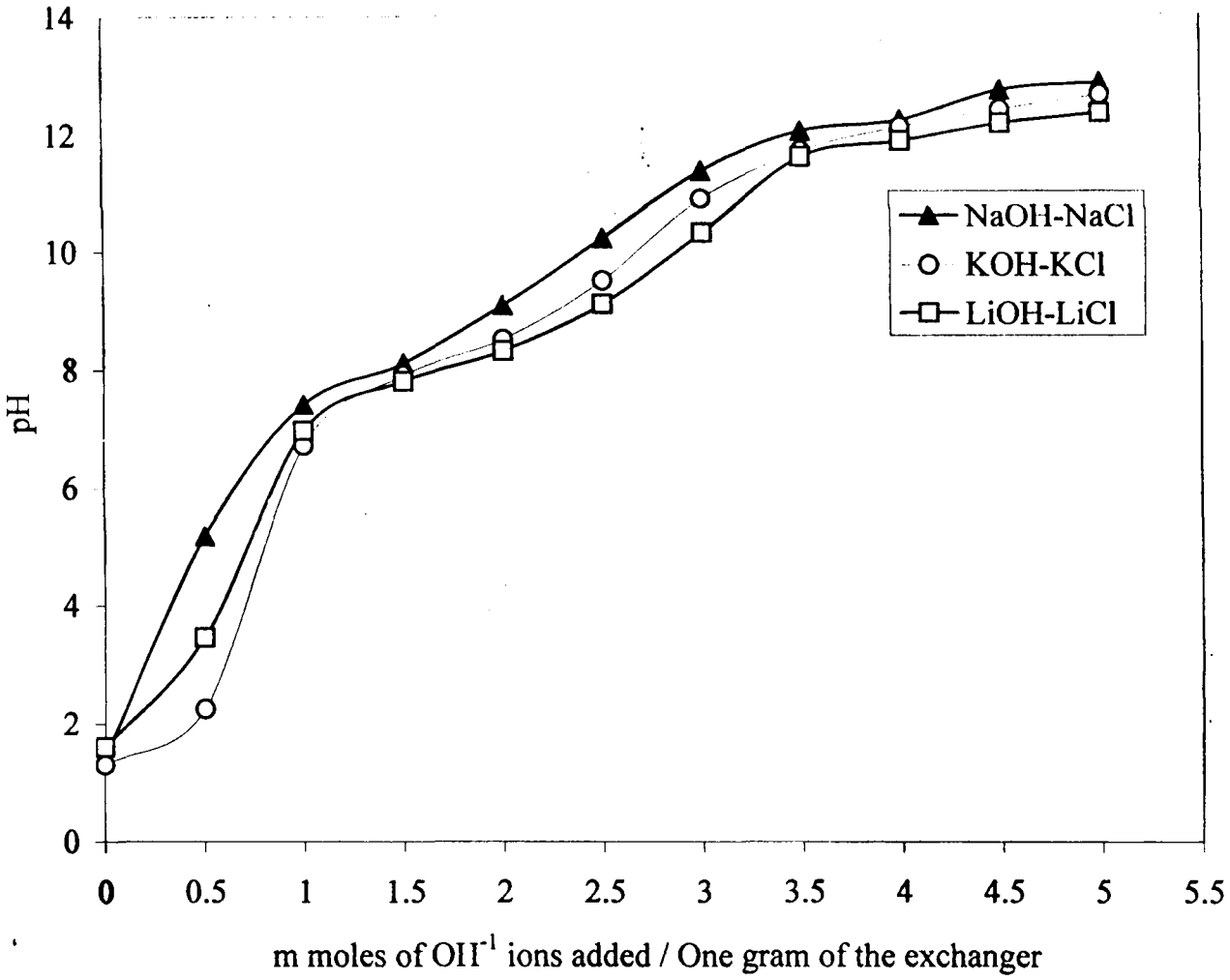

Fig. 3.7. pH-titration curves for polypyrrole Th(IV) phosphate composite cation-exchanger with various alkali metal hydroxides.

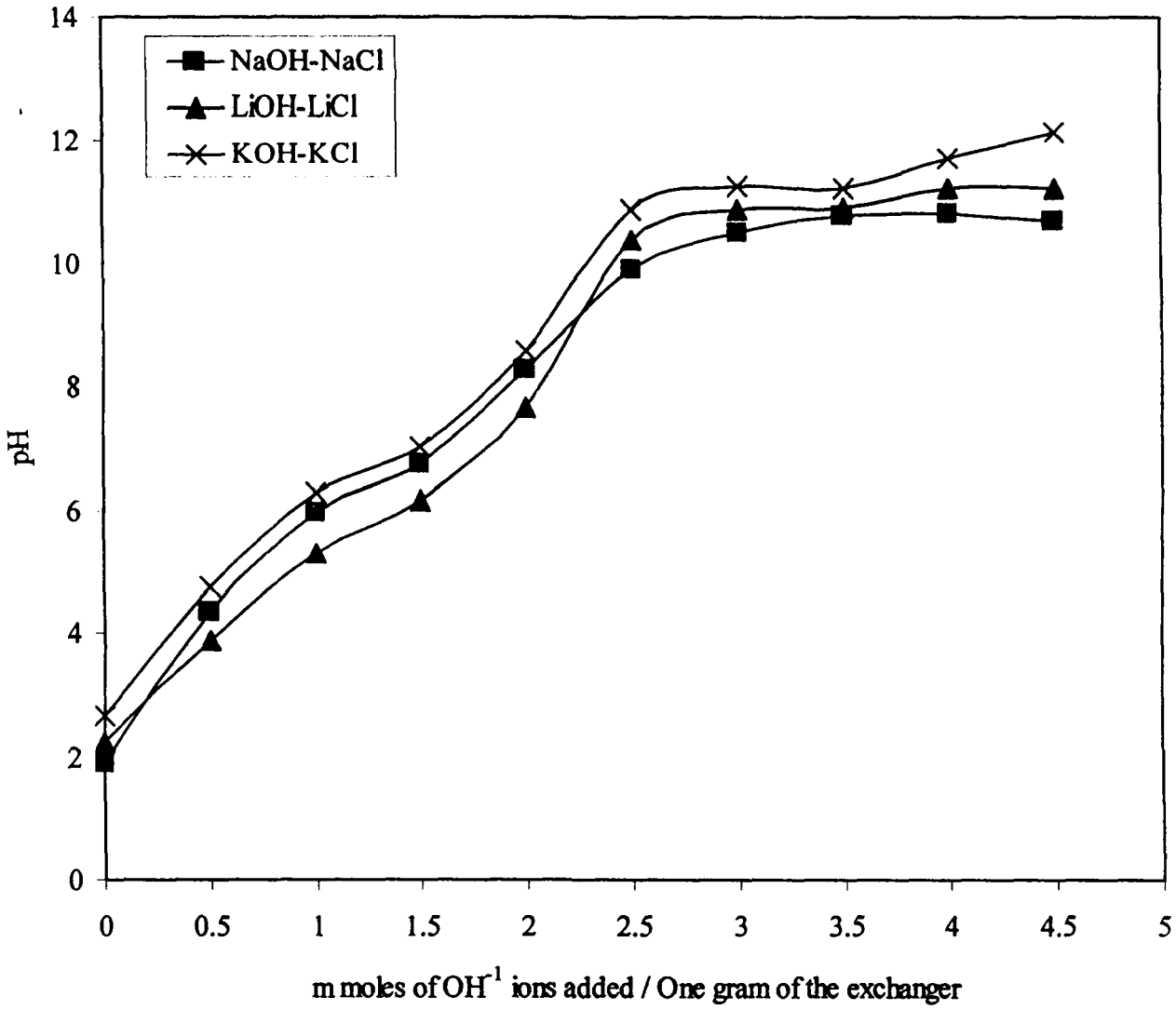

Fig.3.8. pH-titration curves for polyaniline Sn(IV) phosphate composite cation-exchanger with various alkali metal hydroxides.

faster than H^+-Na^+ and H^+-Li^+. The adsorption behavior for alkali metals on polypyrrole Th(IV) phosphate (S-5) material was observed to be in the order of Na(I)>Li(I)>K(I) in acidic pH and Na(I)>K(I)>Li(I) in the basic media, while on polyaniline Sn(IV) phosphate (T-7) was observed in the order of K>Na>Li in acidic pH and K>Li>Na in basic media. The theoretical ion-exchange capacities for the composite cation exchangers sample S-5 and T-7 was found to be ~2.5 meq g^{-1}.

3.3.3. Thermal effect on ion-exchange capacity

On heating at different temperatures for one hour, the ion-exchange capacity of the dried composite cation-exchanger samples (S-5 and T-7) decreased as the temperature increased (Table 3.5). However, polypyrrole Th(IV) phosphate (S-5) was found to possess higher thermal stability as sample maintained 100% of the ion-exchange capacity up to 150 °C and it also retains about 56% of the initial ion-exchange capacity by heating up to 350 °C. Polyaniline Sn(IV) phosphate (T-7) also found to possess higher thermal stability as the sample maintained 100% of the ion-exchange capacity up to 150 °C and it retains about 59% of the initial ion-exchange capacity by heating up to 350 °C. The comparative study of heating effect on Na^+ ion-exchange capacity of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate with those of other ion-exchangers of this class were shown in Fig. 3.9 and Fig. 3.10 respectively. It is clear that these composite cation-exchangers are more thermally stable than others.

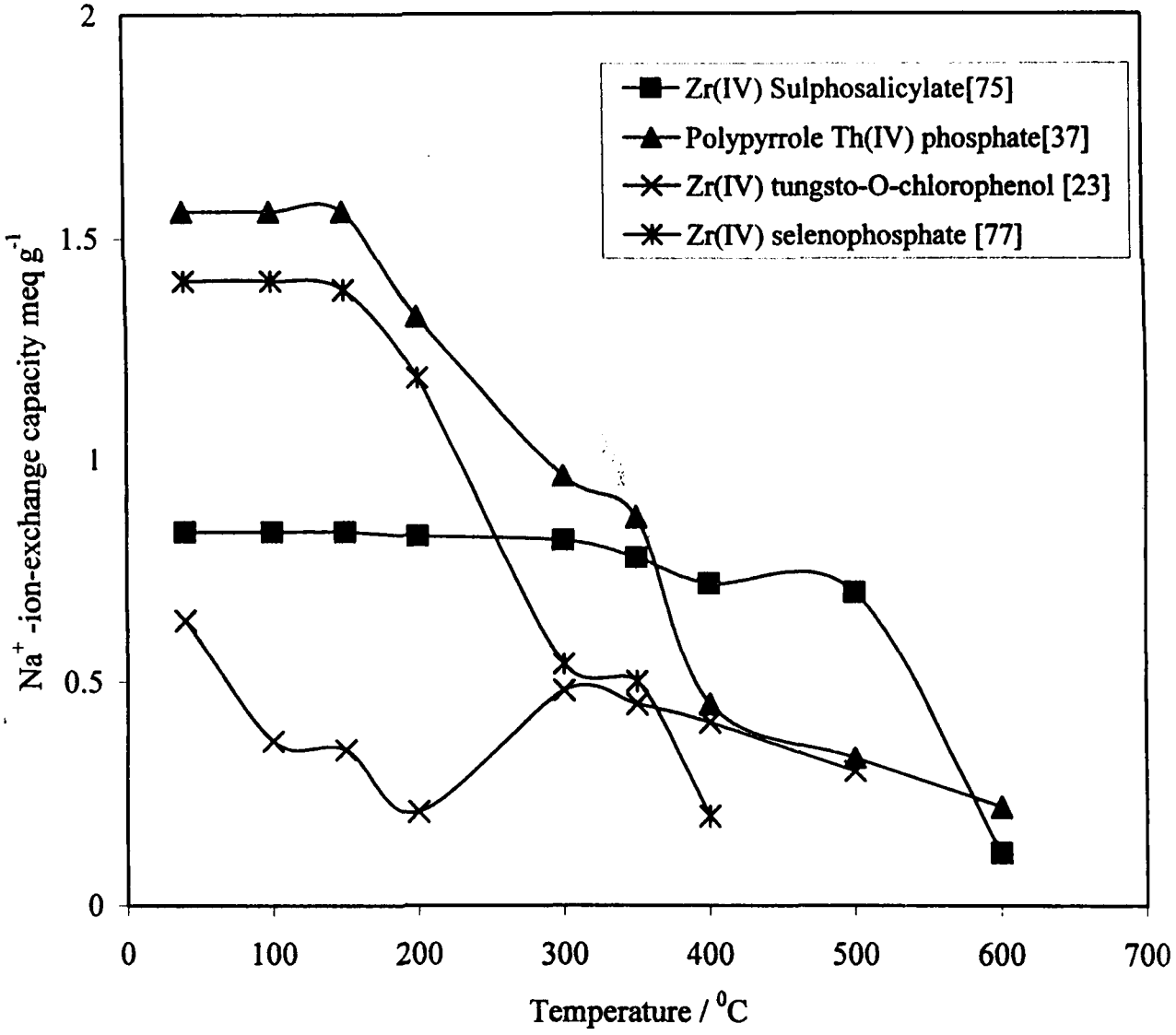

Fig. 3.9. Comparison of heating effect upon ion-exchange capacity of polypyrrole Th(IV) phosphate composite cation-exchanger with those of other cation-exchangers.

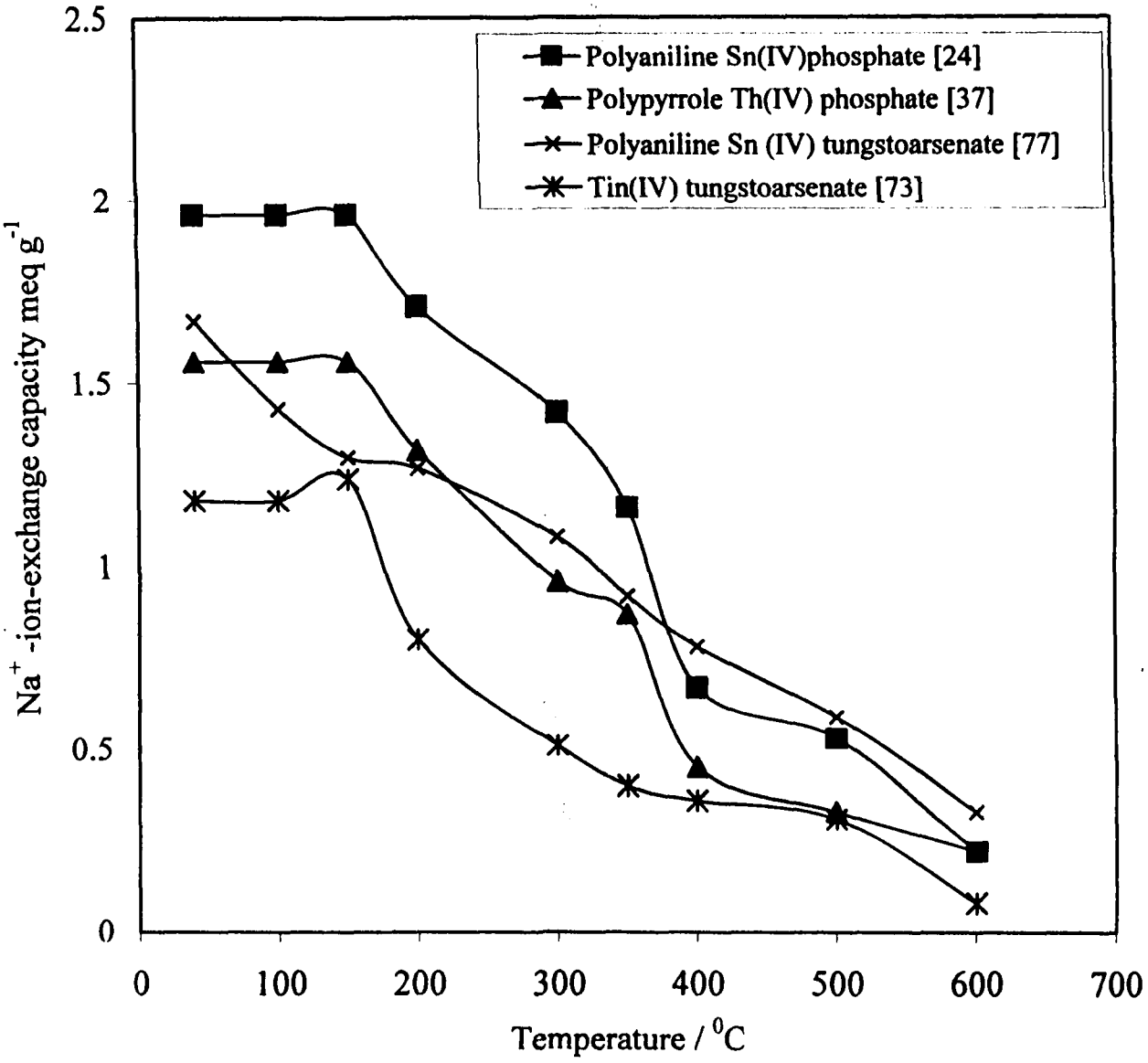

Fig. 3.10. Comparison of heating effect upon ion-exchange capacity of polyaniline Sn(IV) phosphate composite cation-exchanger with those of other cation-exchangers.

3.3.4. Selectivity studies

In order to find out the potentiality of these composite cation-exchange materials sample S-5 and sample T-7 in the separation of metal ions, distribution studies for several metal ions were performed in different solvent systems. It is apparent from the data given in Table 3.9 and 3.10 that the K_d-values can vary with the composition and nature of the contacting solvents. It was observed from the (K_d) values of polypyrrole Th(IV) phosphate (S-5) (Table 3.9) in DMW and 1×10^{-3} M $HClO_4$ that Pb^{2+} is strongly adsorbed; Hg^{2+}, Ba^{2+}, Zr^{4+}, UO_2^{2+}, Ce^{4+}, Tl^{+}, Cu^{2+}, Co^{2+} are also significantly adsorbed while the remaining are partially adsorbed. It was observed from the distribution studies (K_d values) of polyaniline Sn(IV) phosphate (T-7) (Table 3.10) that the Hg^{2+} is highly adsorbed in all solvents, while remaining metal ions are poorly adsorbed. Thus, we can say that both the composite cation-exchangers samples S-5 and T-7 are highly selective for Pb^{2+} and Hg^{2+} ions respectively, and can be very well utilized for the determination and separation of lead and mercury from waste effluents. Consequently, the high uptake of certain metal ion demonstrates not only the ion-exchange properties but also the adsorption and ion-sieve characteristics of the cation-exchanger material.

3.3.5. Separation factors

The separation factor is the proportion of the concentration ratios of the counter ions in the ion-exchanger and the solution. If the ion A is preferred, the factor (α_B^A) is larger than unity, and if B is preferred, the factor is smaller than unity. The numerical value of the (dimension less) separation factor is not affected by the choice

Table 3.9

K_d -values of some metal ions on polypyrrole Th(IV) phosphate column in different solvent systems

Metal Ions	DMW	10^{-3}M $HClO_4$	10^{-2}M $HClO_4$	10^{-1}M $HClO_4$	10^{-2}M HNO_3	10^{-1}M HNO_3	1M HNO_3	10^{-2}M HCl	10^{-1}M HCl	1M HCl
Na^{1}	18	17	12	7	10	7	5	12	7	3
K^{1}	114	80	37	14	31	18	12	41	16	13
Mg^{2+}	20	14	12	-	27	11	9	25	18	11
Ca^{2}	106	80	18	11	13	8	3	73	22	-
Sr^{2}	170	180	53	13	767	50	21	23	17	-
Ba^{2}	650	367	150	114	88	50	36	180	133	56
Cu^{2}	233	133	29	5	11	5	-	24	6	-
Ni^{2}	27	43	25	18	25	17	11	533	500	54
Pb^{2}	900	2000	900	233	1900	300	44	600	90	50
Cd^{2}	37	37	12	8	53	12	-	7	4	-
Mn^{2}	70	43	28	11	33	26	9	23	17	10
Zn^{2}	63	40	13	4	19	11	5	21	-	-
Hg^{2+}	1100	800	767	333	830	600	-	314	67	29
Co^{2}	180	167	155	140	200	160	100	243	140	118
Bi^{3}	20	40	133	100	120	25	-	120	400	-
Al^{3}	20	40	133	100	120	25	-	120	400	-
Fe^{3}	90	88	67	50	169	110	-	140	130	-
La^{3}	87	81	65	61	70	61	-	47	35	-
Ce^{4}	250	200	75	25	40	17	-	50	22	-
Zr^{4}	700	600	400	350	800	750	-	1000	900	-
UO_2^{2+}	833	400	350	233	100	67	20	400	300	150
Tl^{1}	200	500	200	38	71	33	22	50	22	-
Ag^{+}	113	53	33	12	33	21	7	43	29	11

Table 3.10

K_d-values of some metal ions on polyaniline Sn(IV) phosphate column in different solvent systems

Metal ions	DMW	10^{-3}M HNO_3	10^{-2}M HNO_3	10^{-1}M HNO_3	10^{-3}M HCl	10^{-2}M HCl	10^{-1}M HCl	0.1M CH_3COOH + 0.1M CH_3COONa (1:2)	0.1M CH_3COOH + 0.1M CH_3COONa (2:1)	0.1 M HNO_3 + 0.1M NH_4NO_3 (1:1)
Na^+	125	151	200	215	300	120	300	96	54	85
K^+	212	285	321	145	167	200	185	175	158	64
Mg^{2+}	300	271	219	112	300	176	34	316	975	100
Ca^{2+}	141	141	83	34	123	844	46	200	753	371
Sr^{2+}	181	36	15	19	12	-	4	158	94	70
Ba^{2+}	79	48	39	27	225	133	-	113	333	112
Cu^{2+}	771	600	250	283	650	258	38	967	1900	140
Ni^{2+}	237	400	210	150	275	71	67	100	1150	-
Pb^{2+}	2900	2800	2900	2311	2800	1400	250	1300	2200	210
Cd^{2+}	1169	1150	1125	691	311	128	120	375	1428	112
Mn^{2+}	217	160	150	67	133	110	55	145	340	115
Zn^{2+}	386	566	158	88	363	66	62	237	471	-
Hg^{2+}	4300	3500	3500	2900	2200	2360	1180	2600	3700	900
Co^{2+}	400	525	700	700	562	377	420	367	900	150
Bi^{3+}	2300	1500	2000	2300	1400	-	-	650	1400	66
Al^{3+}	1200	900	820	540	700	230	160	250	472	120
Fe^{3+}	700	700	233	205	900	136	116	500	1300	58
La^{3+}	120	85	74	56	62	42	-	148	183	36
Ce^{4+}	1700	1400	1400	766	1000	966	88	1320	3000	72
Zr^{4+}	900	700	350	250	850	729	-	600	850	300
UO_2^{2+}	1000	500	434	329	425	378	269	716	900	412
Tl^+	233	206	200	140	100	260	16	458	135	28
Ag^+	278	118	19	54	34	12	10	22	84	16

of the concentration units. Of course, the separation factor is usually not constant, but depends on the total concentration of the solution, the temperature, and equivalent fraction. On the basis of K_d values, separation factor for some metal ion pairs were calculated and given in Table 3.11 and Table 3.12. These separation factors clarify that the separations are feasible and can be achieved easily.

3.3.6. Ion-exchange kinetics

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Mg(II)-H(I), Ca(II)-H(I), Sr(II)-H(I), Ba(II)-H(I), Ni(II)-H(I), Cu(II)-H(I), Mn(II)-H(I) and Zn(II)-H(I). The particle diffusion-controlled phenomenon is favored by a high metal ion concentration, a relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture.

The infinite time of exchange is the time necessary to obtain equilibrium in an ion exchange process. The ion-exchange rate becomes independent of time after this interval. Fig. 3.1 and Fig. 3.2 shows that 20 and 25 min were required for the establishment of equilibrium at 33 °C for Mg^{2+}-H^+ exchange on polypyrrole Th(IV) phosphate (S-5) and polyaniline Sn(IV) phosphate (T-7) respectively. Similar behavior was observed for Ca^{2+}-H^+, Sr^{2+}-H^+, Ba^{2+}-H^+, Ni^{2+}-H^+, Cu^{2+}-H^+, Mn^{2+}-H^+ and Zn^{2+}-H^+ exchanges. Therefore, 20, and 25 min were assumed to be the infinite time of exchange for the systems.

A study of the concentration effect on the rate of exchange at 33 °C showed that the initial rate of exchange was proportional to the metal ion concentration at and

Table 3.11

Separation factors of different metal ions on polypyrrole Th(IV) phosphate composite cation-exchange material

Separation factor	DMW	10^{-3} M $HClO_4$	10^{-2} M HNO_3
α_{Zn}^{Pb}	14.3	50.0	100.0
α_{Mg}^{Pb}	45.0	142.9	70.4
α_{Al}^{Pb}	45.0	50.0	15.8
α_{Zn}^{Hg}	17.5	20.0	43.7
α_{Fe}^{Hg}	12.2	9.1	4.9
α_{Cd}^{Pb}	24.3	54.1	35.9
α_{Cu}^{Pb}	3.9	31.0	172.7
α_{Ni}^{Pb}	33.3	46.5	76.0

Table 3.12

Separation factors of different metal ions on polyaniline Sn(IV) phosphate composite cation-exchange material

Separation factor	DMW	10^{-2} M HNO_3	10^{-1} M HNO_3	10^{-1} M HCl	0.1M CH_3COOH + 0.1M CH_3COONa (2:1)
α_{Cu}^{Hg}	5.6	14.0	10.3	31.1	2.7
α_{Ni}^{Hg}	18.1	16.7	19.3	17.6	26.0
α_{Cd}^{Hg}	3.7	3.1	4.2	9.8	6.9
α_{Co}^{Hg}	10.8	5.0	4.1	2.8	7.1
α_{Al}^{Hg}	3.6	4.3	5.4	7.4	10.4

above 0.02 M for polypyrrole Th(IV) phosphate, S-5 (Fig. 3.11) and polyaniline Sn(IV) phosphate, T-7 (Fig. 3.12) respectively. Below the concentration of 0.02 M; the film diffusion was more prominent for each material. Plots of $U(\tau)$ versus time (t) (t in min), for all metal ions (Fig. 3.13 and Fig 3.14) indicated that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with an increase in temperature and the uptake decreased with time. Each value of $U(\tau)$ will have a corresponding value of τ, a dimensionless time parameter.

On the basis of the Nernst-Planck equation, the numerical results can be expressed by explicit approximation [78-80]:

$$U(\tau) = \{ 1 - \exp [\pi^2 (f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2} \quad \ldots\ldots 3.5$$

where τ is the half time of exchange $= \overline{D}_{H^+} t / r_0^2$, α is the mobility ratio $= \overline{D}_{H^+} / \overline{D}_{M^{2+}}$, r_0 is the particle radius, $\overline{D}_{H^+}$ and $\overline{D}_{M^{2+}}$ are the inter diffusion coefficients of counter ions H^+ and M^{2+} respectively in the exchanger phase. The three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ depend upon the mobility ratio (α) and the charge ratio ($Z_{H^+}/Z_{M^{2+}}$) of the exchanging ions. Thus they have different expressions as given below. When the exchanger is taken in the H^+-form and the exchanging ion is M^{2+}, for $1 \leq \alpha \leq 20$, as in the present case, the three functions have the values-

$$f_1(\alpha) = - \frac{1}{0.64 + 0.36\ \alpha^{0.668}}$$

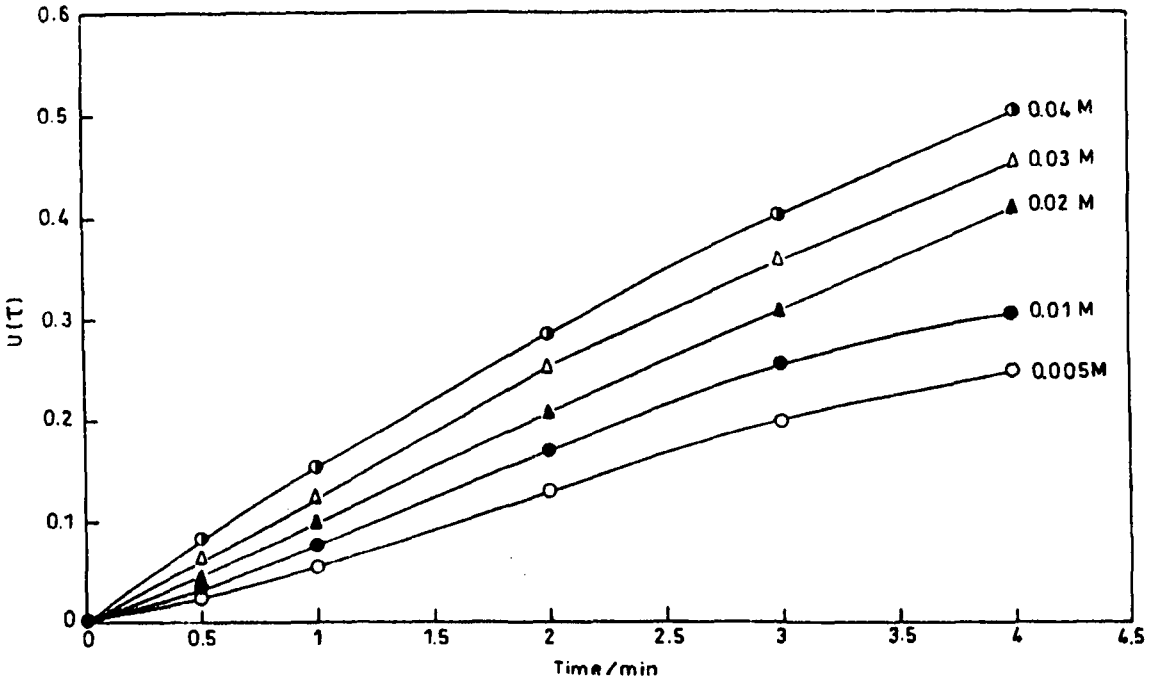

Fig. 3.11. Plots of U(τ) versus t (time) for M(II)-H(I) exchanges using different metal solution concentrations at 33 °C on polypyrrole Th(IV) phosphate composite cation-exchanger.

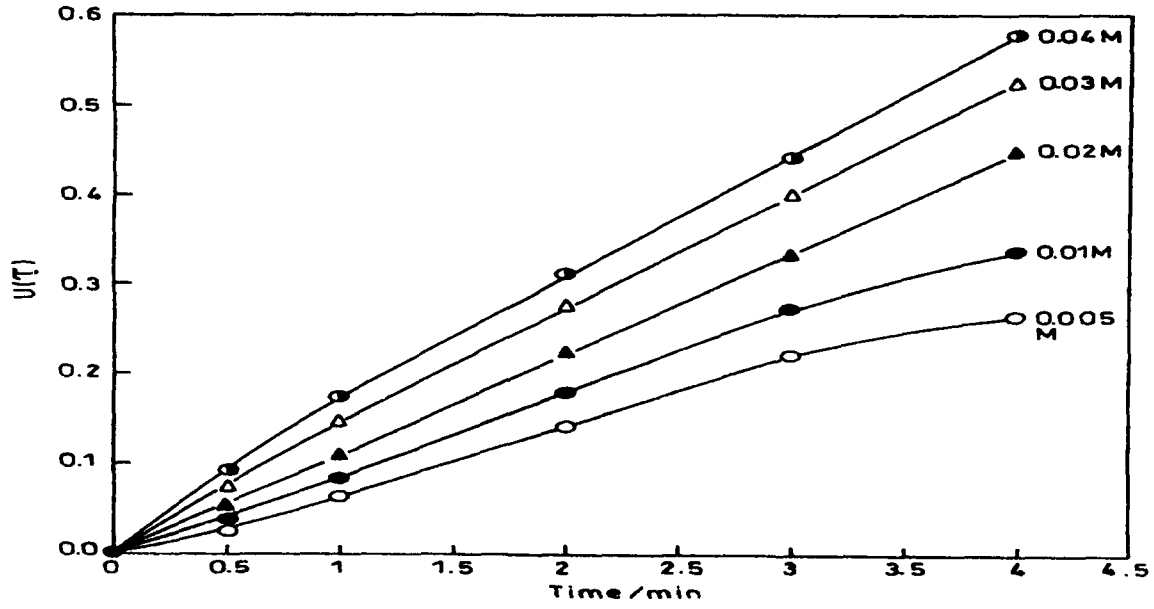

Fig. 3.12. Plots of U(τ) versus t (time) for M(II)-H(I) exchanges using different metal solution concentrations at 33 °C on polyaniline Sn(IV) phosphate composite cation-exchanger.

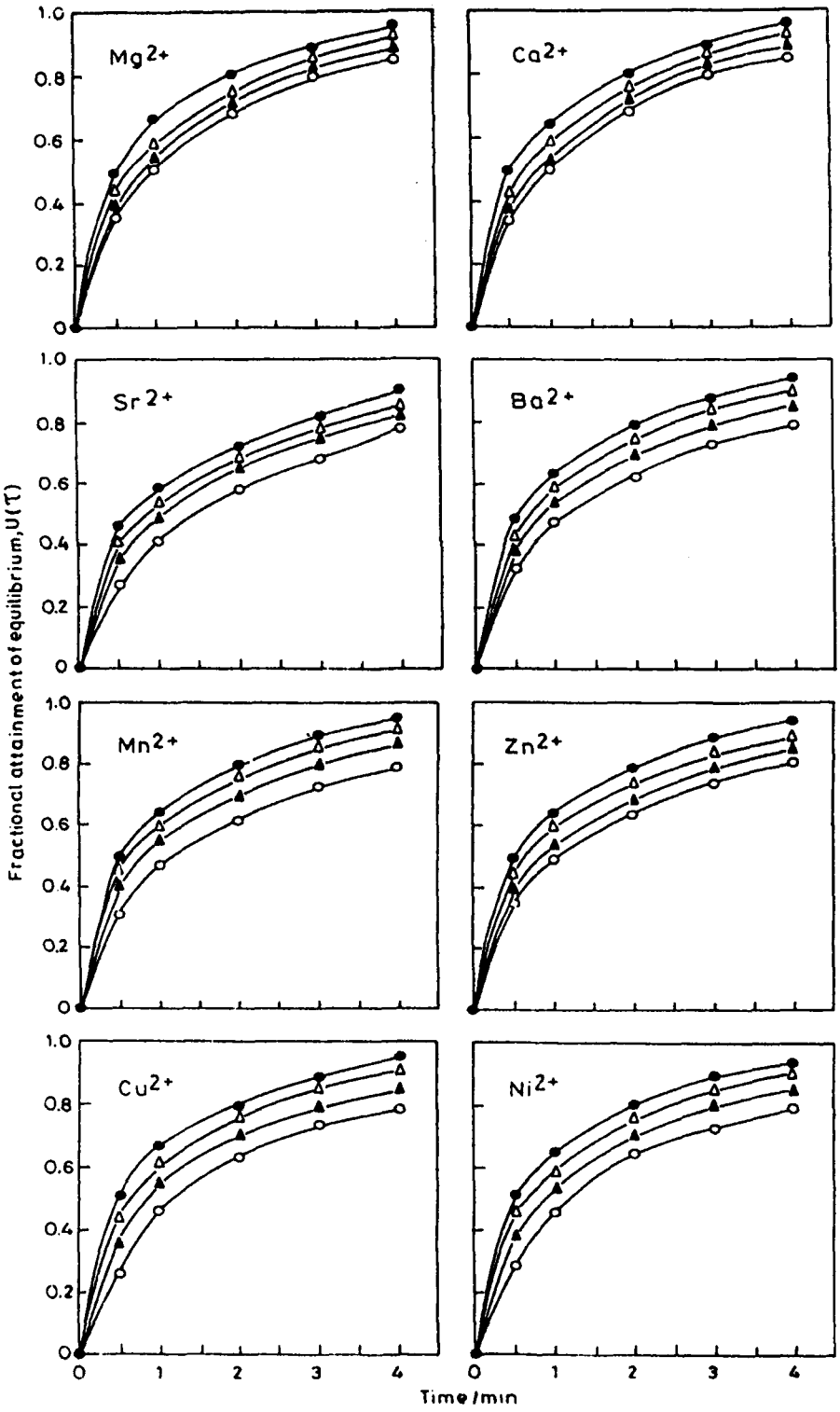

Fig. 3.13. Plots of $U(\tau)$ versus t (time) for different M(II)-H(I) exchanges at different temperatures on polypyrrole Th(IV) phosphate composite cation-exchanger: (□) 25 °C, (▲) 33 °C, (Δ) 50 °C, (●) 65 °C.

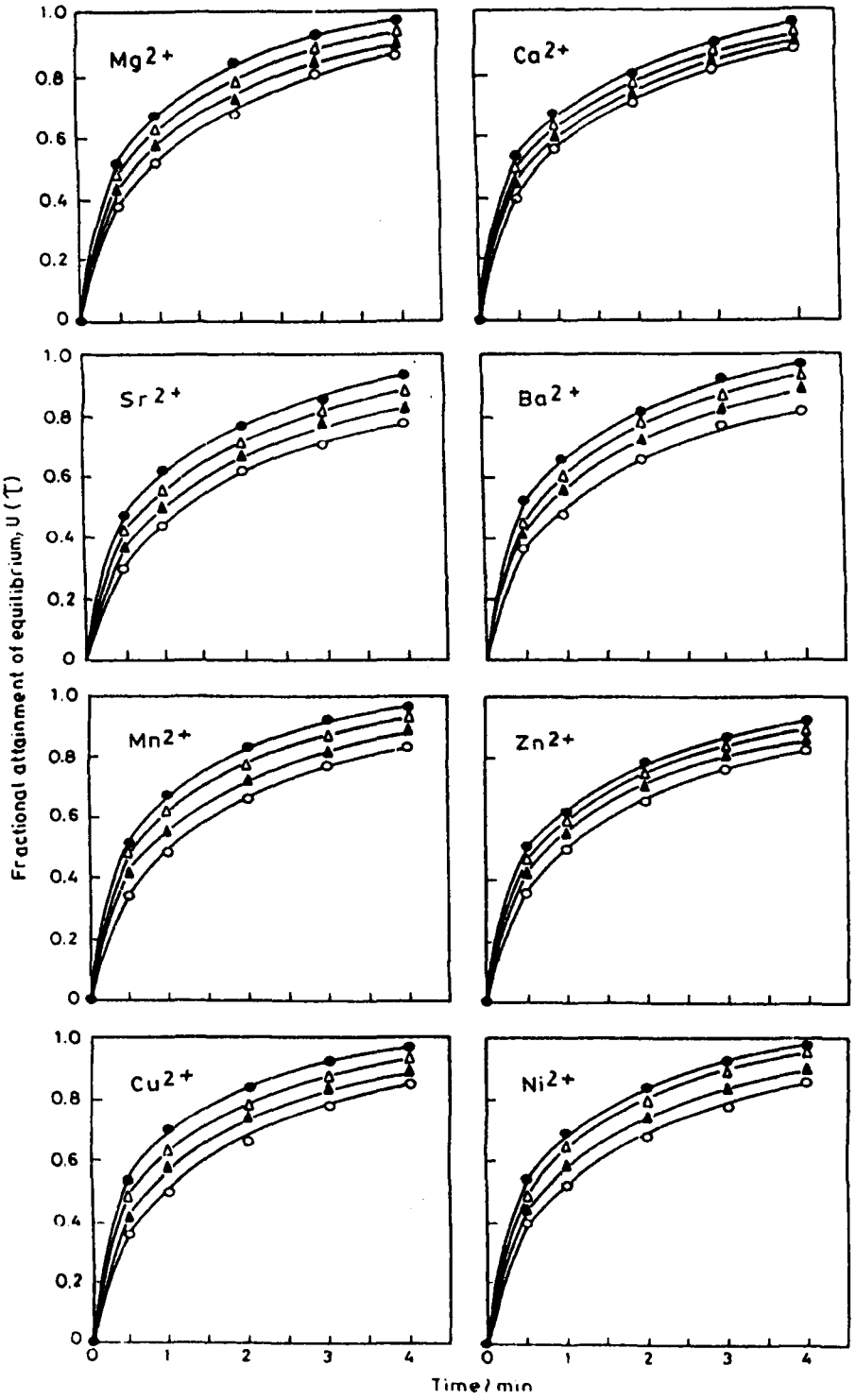

Fig. 3.14. Plots of $U(\tau)$ versus t (time) for different M(II)-H(I) exchanges at different temperatures on polyaniline Sn(IV) phosphate composite cation-exchanger: (□) 25 °C, (▲) 33 °C, (Δ) 50 °C, (●) 65 °C.

$$f_2(\alpha) = - \frac{1}{0.96 - 2.0\ \alpha^{0.4635}}$$

$$f_3(\alpha) = - \frac{1}{0.27 + 0.09\ \alpha^{1.140}}$$

Each value of $U(\tau)$ will have a corresponding value of τ which is obtained on solving equation (3.5) using a computer. The plots of τ versus time (t) at the four temperatures, as shown in Fig. 3.15 and Fig. 3.16, are straight lines passing through the origin, confirming the particle diffusion control phenomenon for M(II)–H(I) exchanges at a metal ion concentration of 0.02 M.

The slopes (S values) of various τ versus time (t) plots are given in Table 3.13. The S values are related to $\overline{D}_{H^+}$ as follows:

$$S = \overline{D}_{H^+} / r_o^2 \qquad \ldots\ldots 3.6$$

The values of $-\log \overline{D}_{H^+}$ obtained by using equation (3.6) plotted against $1/T$ are straight lines as shown in Fig. 3.17 and Fig. 3.18, thus verifying the validity of the Arrhenius relation:

$$\overline{D}_{H^+} = D_o \exp(- E_a / RT) \qquad \ldots\ldots 3.7$$

D_0 is obtained by extrapolating these lines and using the intercepts at the origin. The activation energy (E_a) is then calculated with the help of the equation (3.7), putting the value of $\overline{D}_{H^+}$ at 273 K. The entropy of activation (ΔS^*) was then calculated by substituting D_0 in equation (3.8).

$$D_0 = 2.72 d^2 (kT / h) \exp(\Delta S^* / R) \qquad \ldots\ldots 3.8$$

where d is the ionic jump distance taken as 5×10^{-10} m [81], k is the Boltzmann

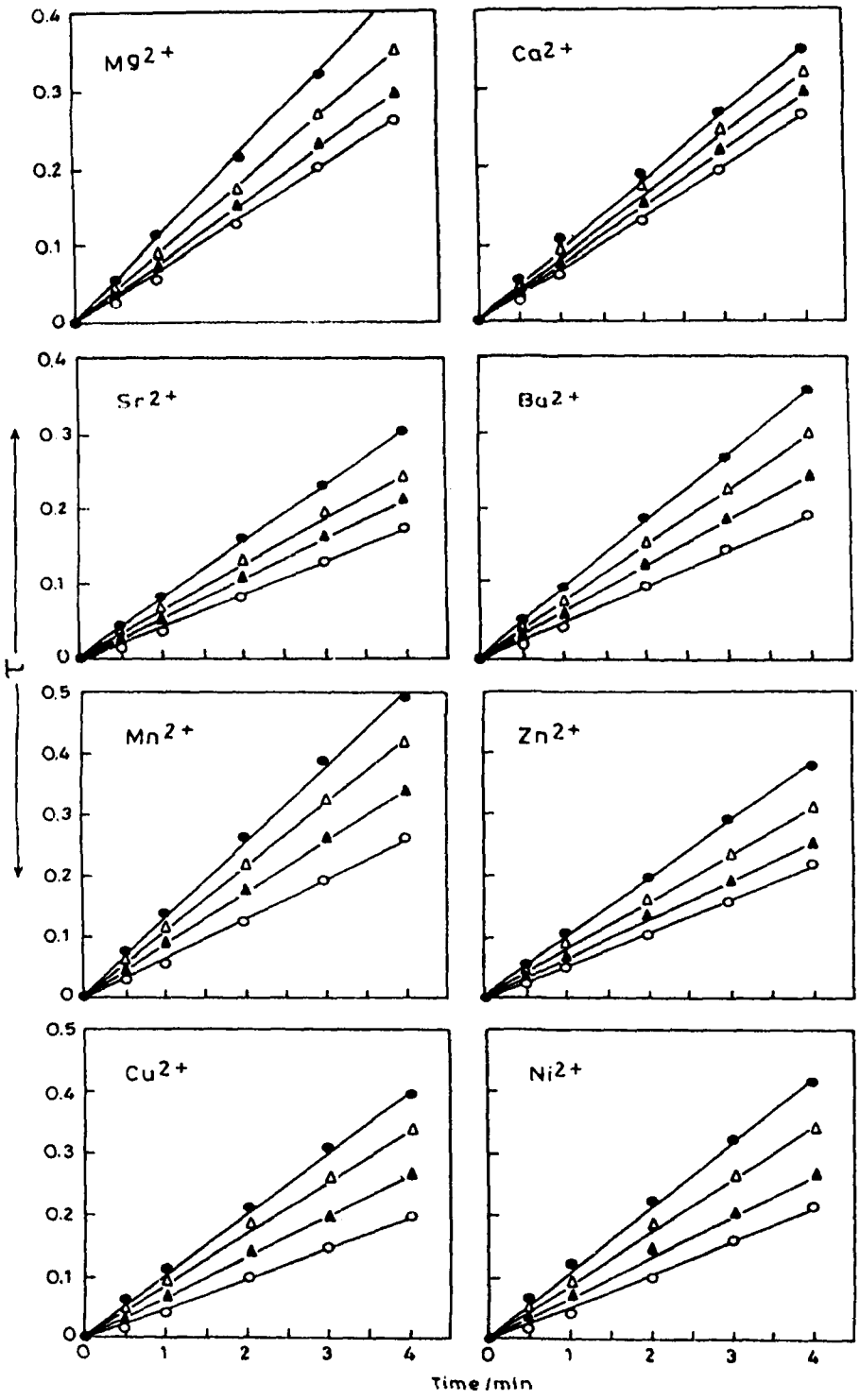

Fig. 3.15. Plots of τ versus t (time) for different M(II)-H(I) exchanges at different temperatures on polypyrrole Th(IV) phosphate composite cation-exchanger: (□) 25 °C, (▲) 33 °C, (Δ) 50 °C, (●) 65 °C.

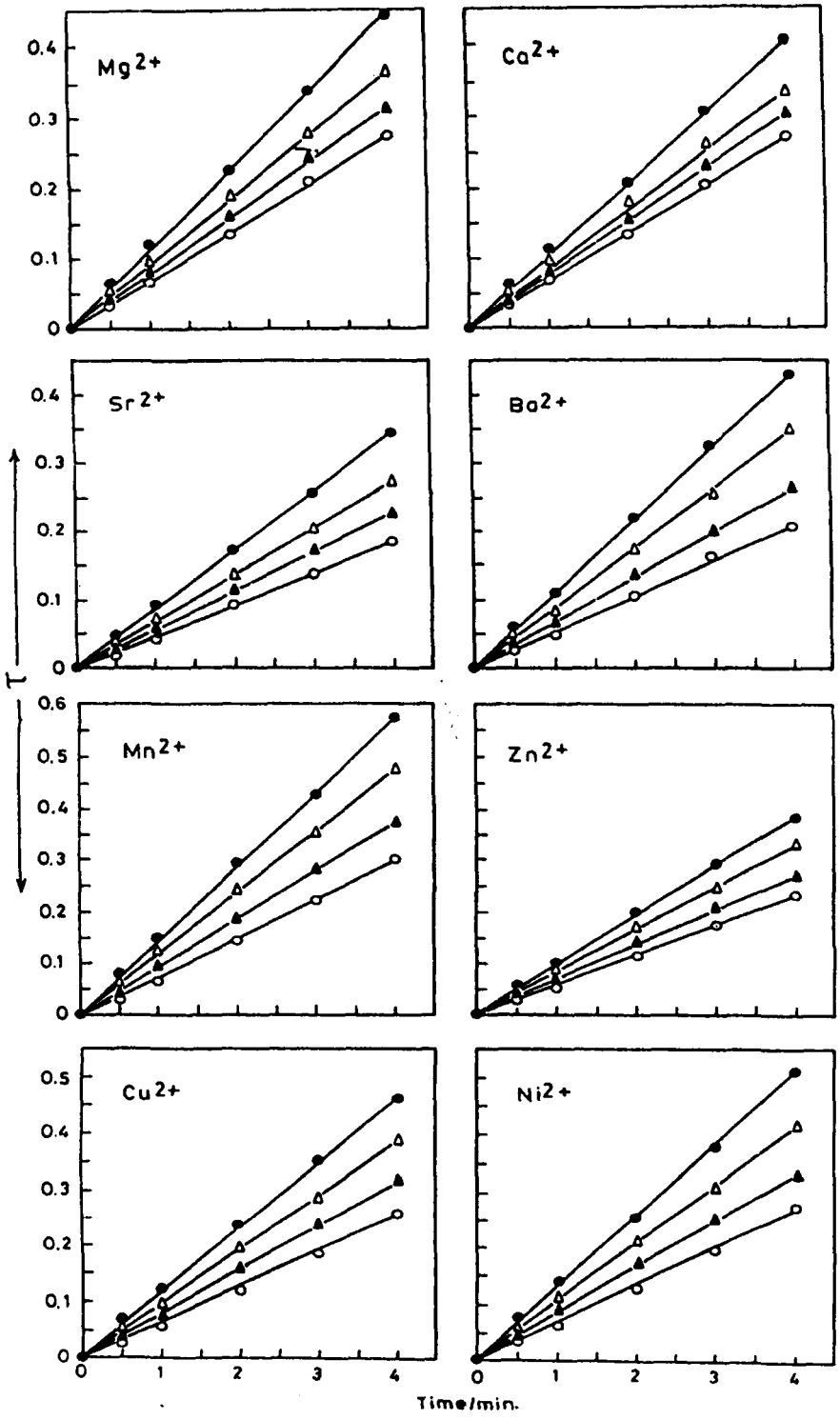

Fig.3.16. Plots of τ versus t (time) for different M(II)-II(I) exchanges at different temperatures on polyaniline Sn(IV) phosphate composite cation-exchanger: : (□) 25 °C, (▲) 33 °C, (Δ) 50 °C, (●) 65 °C.

Table 3.13

Slopes of various τ versus time (t) plots on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers at different temperatures

Migrating ions ⇓	S (s^{-1}) × 10^2							
	Polypyrrole Th(IV) phosphate (S-5)				Polyaniline Sn(IV) phosphate (T-7)			
Temp. ⇒	25 °C	33 °C	50 °C	65 °C	25 °C	33 °C	50 °C	65 °C
Mg(II)	6.48	7.38	8.73	10.61	6.83	7.83	9.18	11.18
Ca(II)	6.48	7.27	8.06	8.88	6.72	7.58	8.51	10.15
Sr(II)	4.21	5.24	6.19	7.62	4.56	5.63	6.79	8.58
Ba(II)	4.70	6.08	7.45	8.93	5.31	6.65	8.63	10.77
Mn(II)	4.85	6.59	8.46	10.10	6.28	7.84	9.59	11.61
Zn(II)	5.23	6.68	8.58	10.62	6.60	8.25	10.32	12.70
Cu(II)	5.36	6.41	7.74	9.68	5.79	6.76	8.29	9.70
Ni(II)	6.35	8.53	10.52	12.73	7.40	9.29	11.87	14.36

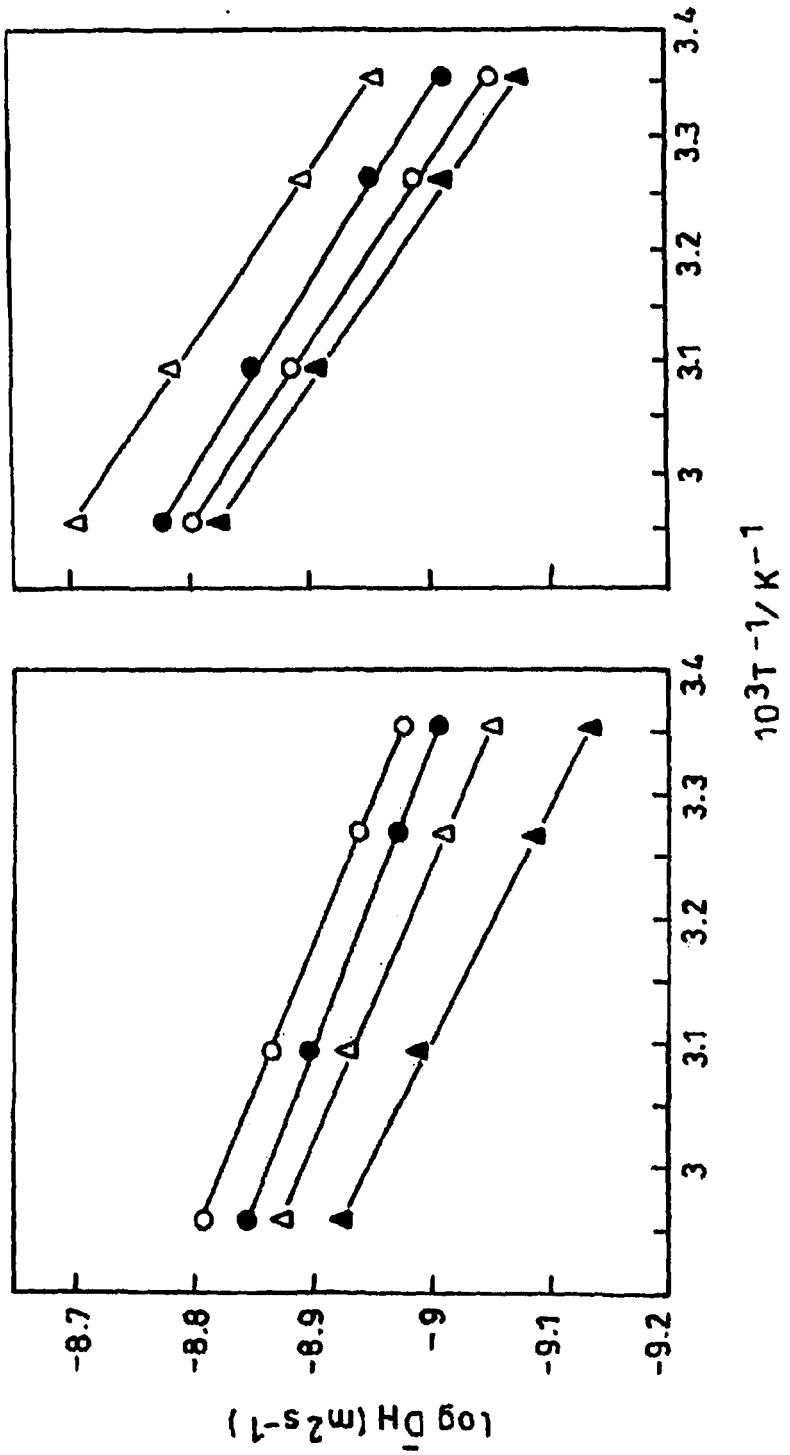

Fig. 3.17. Plots of $-\log \bar{D}_H$ versus $10^3T^{-1}/K^{-1}$ for (a) Mg (II): □, Ca(II): ●, Ba(II): Δ, Sr(II): ▲, and (b) Mn(II): Δ, Ni(II): ●, Cu(II):□, Zn(II): ▲, on polypyrrole Th(IV) phosphate composite cation-exchanger.

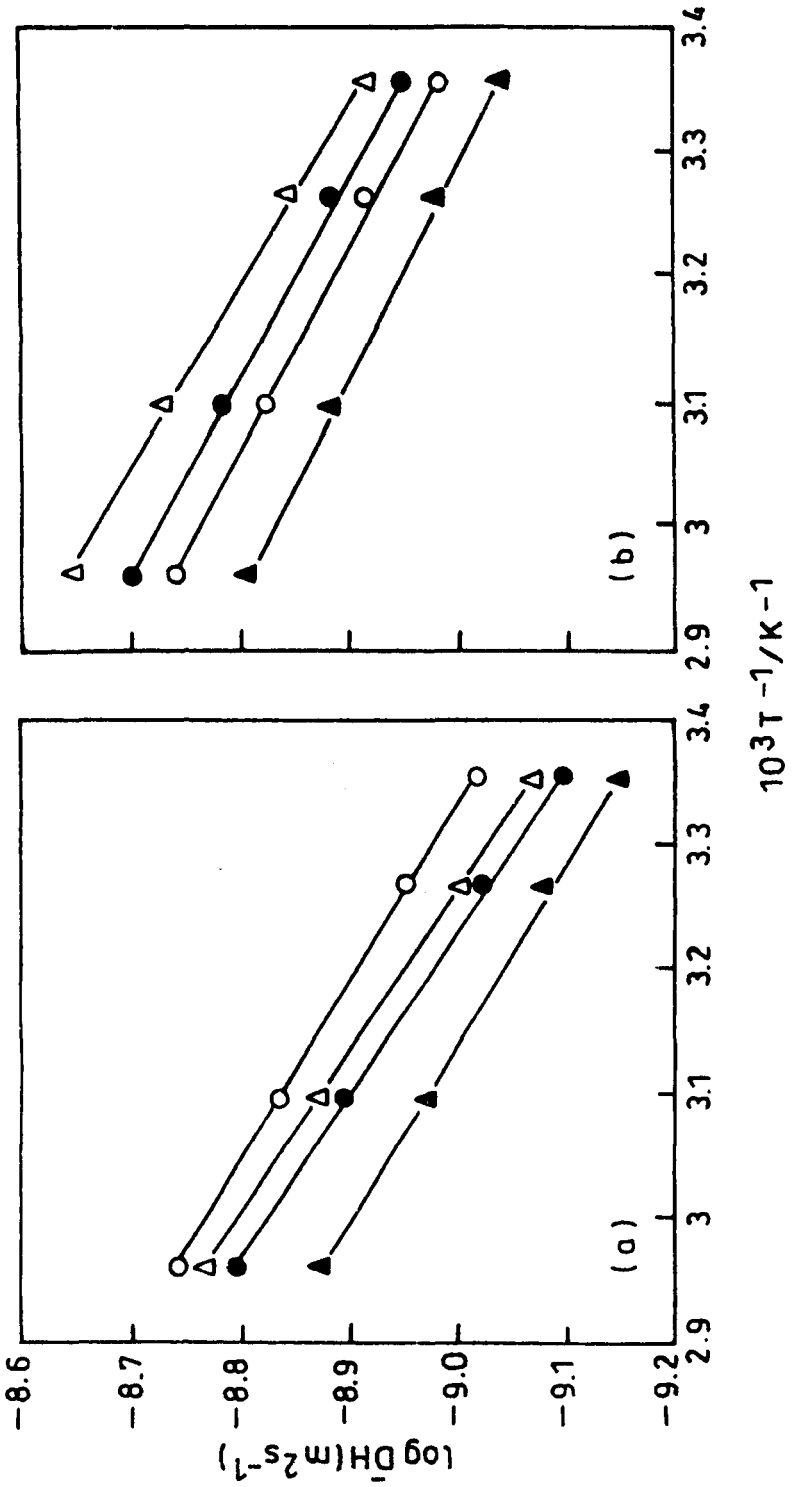

Fig. 3.18. Plots of $-\log \bar{D}_H$ versus $10^3T^{-1}/K^{-1}$ for (a) Mg (II): □, Ca(II): ●, Ba(II): Δ, Sr(II): ▲, and (b) Mn(II): Δ, Ni(II): ●, Cu(II): □, Zn(II): ▲, on polyaniline Sn(IV) phosphate composite cation-exchanger.

constant, R is the gas constant, h is Plank's constant and T is taken as 273 K. The values of the diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation (ΔS^*) thus obtained are summarized in Table 3.14.

The kinetic study reveals that equilibrium is attained faster at a higher temperature (Fig. 3.13 and Fig. 3.14), probably because of a higher diffusion rate of ions through the thermally enlarged interstitial positions of the ion-exchange matrix. The particle diffusion phenomenon is evident from the straight lines passing through the origin for the τ versus time (t) plots, as shown in Fig. 3.15 and Fig. 3.16. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange [M(II) - H(I)] process.

Table 3.14

Values of D_0, E_a and ΔS^* for the exchange of H(I) with some metal ions on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers

Metal ion exchange with H(I)	10^9Ionic mobility /$m^2\ V^{-1}\ s^{-1}$	10^2Ionic radii / nm	Polypyrrole Th(IV) phosphate (S-5)			Polyaniline Sn(IV) phosphate (T-7)		
			10^8D_0 /$m^2\ s^{-1}$	10^2E_a /kJ mol^{-1}	ΔS^* /J K^{-1} mol^{-1}	10^7D_0 /$m^2\ s^{-1}$	10^2E_a /kJ mol^{-1}	ΔS^* /J K^{-1} mol^{-1}
Mg(II)	55	7.8	2.86	42.71	- 1.21	1.88	68.24	- 0.39
Ca(II)	62	10.6	2.39	41.29	- 1.29	2.57	74.53	- 0.26
Sr(II)	62	12.7	4.61	53.85	- 1.00	1.36	67.92	- 0.53
Ba(II)	66	14.3	2.83	44.80	- 1.22	2.79	74.95	- 0.22
Mn(II)	57	7.0	11.34	62.70	- 0.61	1.16	61.04	- 0.60
Zn(II)	52	7.8	9.80	59.67	- 0.68	1.55	63.92	- 0.48
Cu(II)	56	8.3	12.00	64.16	- 0.59	0.80	57.81	- 0.78
Ni(II)	55	9.1	16.26	64.56	- 0.46	2.27	67.60	- 0.31

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Chapter 4

Electrical Conductivity Measurement Studies of "Organic-inorganic" Composites Polypyrrole Th(IV) Phosphate & Polyaniline Sn(IV) phosphate

Chapter 4

4.1. Introduction

The possibility of combining the properties of organic and inorganic compounds in a unique material is an old challenge. Actually, research on hybrid organic/inorganic materials is an expending area in the materials science [1-10]. Therefore, organic-inorganic composite materials are of intensive interest in the field of contemporary materials chemistry as these materials can exhibit synergetic extraordinary properties such as electrical, magnetic and optical properties [11], which arise from the synergism between the properties of the organic and inorganic components. Thus, these materials have gained much interest due to their remarkable change in properties such as mechanical [12], thermal [13–16], electrical [17], and magnetic [18] compared to pure organic polymers. Additionally, the properties of the composite materials depend on the morphology of the phases *viz.* organic and/or inorganic network, which has to be controlled over several length scales. Therefore, the development of such materials is a 'land of multidisciplinarity' [1], where chemists, physicists, material scientists and engineers have to work closely together to fully exploit this technical opportunity for creating materials and device with benefits of the best of the two worlds namely inorganic and organic.

One important class of hybrid materials is that in which the inorganic fraction is composed by conducting polymers, in which new inorganic lattice structures are formed, resulting from cooperative interactions between the organic and inorganic

components. In all cases, there is promise of developing new materials with properties not seen in purely organic or purely inorganic solids. In general, the formation of hybrids between conducting polymers and inorganic solids aims to obtained composite materials with synergetic or complementary behaviors between the polymer and the inorganic matrices. The properties of the designed composites will depend both on the characteristics of the polymers and on the nature of the inorganic matrices. This approach can be very useful to obtain materials with predominant properties. The electrical conductivity of the conducting polymers is due to the conjugated backbone, which is totally responsible for electro-active character. The electrically conducting polymers are the electrochromic materials with chemically active surface [19-22]. But they are chemically sensitive and have poor mechanical properties and pose processibility problems. The inherent instability is also due to highly unsaturated backbone of conjugated polymers. Stability problems have, therefore, caused many research groups to search for conjugated polymers of high stability. To meet the requirements of stability of materials of improved performance, explosive research is going on to synthesize the composites of '*organic-organic*' and '*organic-inorganic*' nature. In the view of the above-mentioned facts, researchers have shown much interest in the study of electrically conducting behavior of 'organic-inorganic' composite materials [23-30].

In this chapter, we report the preparation of composites of conducting polymers (polypyrrole and polyaniline) and polyvalent metal acid salts of (Th(IV) phosphate and Sn(IV) phosphate) by mixing different amounts (vol.%) of organic monomers with fixed volume of inorganic precipitates. The electrical conductivity behavior of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite systems with increasing temperature was measured by using 4-in-line-probe dc electrical conductivity measuring instrument.

4.2. Experimental

4.2.1. Reagents and chemicals

The main reagents used for the synthesis were: Thorium nitrate ($Th(NO_3)_4$. $5H_2O$, 99%, and Stannic chloride, $SnCl_4.5H_2O$, 97.5%, CDH India Ltd.), Phosphoric acid (H_3PO_4, 88-93% Loba Chemie India Ltd.), Di-sodium hydrogen orthophosphate (Na_2HPO_4, CDH (India). Pyrrole (C_4H_4NH, 98%, E-Merck India Ltd.), Toluene ($C_6H_5CH_3$, 95% CDH India Ltd.), Ferric chloride ($FeCl_3$, 96%, CDH India Ltd.), Aniline ($C_6H_5NH_2$, 99%, Qualigens India Ltd.), Potassium persulphate ($K_2S_2O_8$, 98%, CDH India Ltd.), Hydrochloric acid HCl, 35% and Nitric acid HNO_3, 35%, E-Merck India Ltd.). All other reagents and chemicals were of analytical reagent grade.

4.2.2. Instrumentation

- A four-in-line probe electrical conductivity measuring instrument Scientific Equipment (Roorkee, India); was used for measuring dc electrical conductivity.
- A hydraulic pressure instrument was used for making pellets of sample materials.
- An electronic balance (digital) - Sartorius (Japan), model 21 OS.
- A mortar pastel.
- A micrometer having least counts 0.01 mm.

4.2.3. Preparation of the reagent solutions

0.1 M solutions of thorium nitrate, $Th(NO_3)_4.5H_2O$ and stannic chloride, $SnCl_4.5H_2O$ were prepared in 1 M HNO_3 and 4 M HCl respectively, while orthophosphoric acid, H_3PO_4 solutions of different molarities, 0.1 M di-sodium hydrogen orthophosphate, Na_2HPO_4 and 0.1 M $FeCl_3$ solutions were prepared in demineralized water (DMW). Pyrrole solutions of 3.33 to 40% (vol.%) were prepared in toluene. Solutions of 2 to 20% (vol.%) doubly distilled aniline ($C_6H_5NH_2$) and 0.1 M potassium persulphate ($K_2S_2O_8$) were prepared in 1 M HCl.

4.2.4. Preparation of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composites

Various samples of 'polypyrrole Th(IV) phosphate' and polyaniline Sn(IV) phosphate were prepared through the method described in Chapter – 2, Section - 2.2.3 (Table 2.1 and Table 2.2) by mixing different concentrations of pyrrole (approximately 3.33 to 40 %; vol.%) and aniline (2 to 20% (vol.%) monomers into fixed volume of inorganic precipitates of Th(IV) phosphate and Sn(IV) phosphate, respectively as given in Table 4.1 and Table 4.2.

4.2.5. Electrical conductivity measurement studies

The measurements of electrical conductivities were carried out on various samples of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composites.

Table 4.1

Preparation of various samples of polypyrrole Th(IV) phosphate composite material with fixed volume of inorganic precipitates

Samples	Mixing volume ratios (v/v)				Appearance of the beads after drying
	0.1 M $Th(NO_3)_4.5H_2O$ in 1 M HNO_3	H_3PO_4	Pyrrole in toluene (Vol. %)	0.1 M $FeCl_3$	
PT-1	5	2 (2 M)	0.30 (3.33%)	2	Blackish granular
PT-2	5	2 (2 M)	0.30 (6.66 %)	2	Blackish granular
PT-3	5	2 (2 M)	0.03 (10 %)	2	Blackish granular
PT-4	5	2 (2 M)	0.30 (13.33 %)	2	Blackish granular
PT-5	5	2 (2 M)	0.30 (16.66 %)	2	Blackish granular
PT -6	5	2 (2 M)	0.30 (20 %)	2	Blackish granular
PT-7	5	2 (2 M)	0.30 (23.33 %)	2	Blackish granular
PT-8	5	2 (2 M)	0.30 (26.66 %)	2	Blackish granular
PT-9	5	2 (2 M)	0.30 (30 %)	2	Blackish granular
PT-10	5	2 (2 M)	0.30 (33.33 %)	2	Blackish granular
PT-11	5	2 (2 M)	0.30 (36.66 %)	2	Blackish granular
PT-12	5	2 (2 M)	0.30 (40 %)	2	Blackish granular

Table 4.2

Preparation of various samples of polyaniline Sn(IV) phosphate composite material with fixed volume of inorganic precipitates

Samples	Mixing volume ratios (v/v)					Appearance of the yield after drying
	0.1 M $SnCl_4.5H_2O$ in 4 M HCl	0.1 M Na_2HPO_4 in DMW	pH of the inorganic precipitate	0.1 M $K_2S_2O_8$ in 1 M HCl	Aniline in 1 M HCl (vol.%)	
PS-1	2	3	1.0	1	1 (2%)	Greenish granular
PS-2	2	3	1.0	1	1 (4%)	Greenish granular
PS-3	2	3	1.0	1	1 (6%)	Greenish granular
PS-4	2	3	1.0	1	1 (8%)	Greenish granular
PS-5	2	3	1.0	1	1 (10%)	Greenish granular
PS-6	2	3	1.0	1	1 (12%)	Greenish granular
PS-7	2	3	1.0	1	1 (14%)	Greenish granular
PS-8	2	3	1.0	1	1 (16%)	Greenish granular
PS-9	2	3	1.0	1	1 (18%)	Greenish granular
PS-10	2	3	1.0	1	1 (20%)	Greenish granular

4.2.5.1. Treatment with HCl solution (acidic doping)

Polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite materials were treated with 0.5 M aqueous solution of HCl to induced protonic acid doping. The materials were washed for excess HCl with doubly distilled water repeatedly till the filtrate gave negative test for hydrogen ions. Then the samples were dried at 50 °C in the oven for 48 hours.

4.2.5.2. Sample (pellet) preparation

The dried sample materials were finely ground in a mortar pastel and then taken into a die with spatula. The pellets of different sample materials of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate for electrical conductivity measurement were made at room temperature with the help of a hydraulic pressure instrument, at 25 KN pressure for 20 minutes. Thickness of each sample was measured by a micrometer at five different points and the average thickness was taken as the thickness of the pellet sample.

4.2.5.3. Instrumental method of electrical conductivity measurements

Four probe dc electrical conductivity measurements with increasing temperature for the representative samples of polypyrrole Th(IV) phosphate (PT-10) and polyaniline Sn(IV) phosphate (PS-5) (as prepared and HCl treated) were performed on pressed pellets by using a 4-in-line-probe dc electrical conductivity measuring technique.

The sample to be tested was placed on the base plate of four-probe arrangement and the probes allowed to rest in the middle of the sample. A very gentle

pressure was applied on the probes and then it was tightened in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply was then switched on, the temperature was allowed to increase gradually with current, and voltage was recorded with rise in temperature.

4.2.5.4. Thermal stability of composites in terms of dc electrical conductivity retention

4.2.5.4.1. Isothermal technique

The isothermal stability of the polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite materials in terms of dc electrical conductivity retention were studied under isothermal condition using 4-in-line-probe dc electrical conductivity measuring instrument. This study was carried out at 50, 70, 90, 110, 130 and 150 °C on the selected composite samples (PT-10, and PS-5, HCl treated). The electrical conductivity measurements were done at an interval of 15 minutes.

4.2.5.4.2. Cyclic technique

The thermal stability of the polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composites in terms of electrical conductivity retention were also studied by repeatedly measuring dc electrical conductivity on pressed pellets of composite sample (PT-10, PS-5, HCl treated) with increasing temperature from 30 to 200 °C. The measurements were repeated in this temperature range for 5 times at an interval of 45 minutes.

4.2.5.5. Environmental stability of the conductivity of composites

The stability of the polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite materials (PT-10, and PS-5, HCl treated) in terms of electrical conductivity retention was studied by repeatedly measuring 4-in-line probe dc electrical conductivity at room temperature on pressed pellets at an interval of five days by short-term exposure to laboratory air.

4.3. Results and Discussions

In this chapter, various samples of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate electrically conducting 'organic-inorganic' composite materials were chemically prepared by the incorporation of polypyrrole and polyaniline conducting polymers into the inorganic matrices of fibrous type Th(IV) phosphate and Sn(IV) phosphate, respectively *i.e.* by mixing different concentrations (vol.%) of organic monomers into the fixed volume of inorganic precipitates. Among these, sample PT-10 and PS-5 (Table 4.1 and Table 4.2) were selected for detail electrical conductivity studies.

These composite materials contain two components *viz.* inorganic and organic. The inorganic components of the composites are the efficient ion-exchange materials whereas organic components, polypyrrole or polyaniline are good electronically conducting polymers. In general, a high electrical conductivity of conductive polymers is attained by dopant, which stabilize the polaron and bipolaron states as counter anions [31-34].

Thus, the dc electrical conductivity of composite ion-exchange materials is due to the presence of sufficient amount of the conducting polymer and basically it is electronic conduction contributed by the conducting components, *i.e.* polypyrrole and polyaniline by the charge-transfer reaction between polypyrrole and polyaniline component of the composites and doping agents, HCl, respectively as given:

[Polypyrrole Th(IV) phosphate] + n HCl → [Polypyrrole (n H^+)(n Cl^-) Th(IV) phosphate] 4.1

and

[Polyaniline Sn(IV) phosphate] + n HCl → [Polyaniline (n H^+)(n Cl^-) Sn(IV) phosphate] 4.2

Controlling the doping process (*i.e.* treatment with aqueous solution of HCl), the electrical conductivity of these materials could be varied from insulator, through semiconductor to metal range and *vice-versa*. Schöllhörn and Zagefka [35] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides, which has further been supported by the work of Foot and Shaker [36]. On the basis of the disproportionation reaction of ammonia as suggested by above workers (equation-4.3), Mohammad [37] also has suggested an analogous disproportionation reaction for water (equation-4.4).

$$8\,NH_3 \rightarrow 6\,NH_4^+ + 6\,e^- + N_2 \qquad \ldots\ldots 4.3$$

$$6\,H_2O \rightarrow 4\,H_3O^+ + 4\,e^- + O_2 \qquad \ldots\ldots 4.4$$

The basic strength of water is very low, hence does not act as undoping agent in case of polypyrrole and polyaniline. However, the neutralization reactions to undope polypyrrole and polyanilne within polypyrrole Th(IV) phosphate and polyaniline Sn(IV) composite cation-exchange materials by ammonia may be suggested as under-

$$[\text{Polypyrrole } (n\,H^+)(n\,Cl^-)\text{ Th(IV) phosphate}] + n\,NH_4^+ + n\,e^- \rightarrow [\text{Polypyrrole Th(IV) phosphate}] + n\,NH_4Cl \qquad \ldots\ldots 4.5$$

and

$$[\text{Polyaniline } (n\,H^+)(n\,Cl^-)\text{ Sn(IV) phosphate}] + n\,NH_4^+ + n\,e^- \rightarrow [\text{Polyaniline Sn(IV) phosphate}] + n\,NH_4Cl \qquad \ldots\ldots 4.6$$

4.3.1. Electrical conductivity measurements

Electrical conductivities of the pellets of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite samples were determined from the measurement of conductivity of the samples using the four-probe method of conductivity measurement for semiconductors. That is the most satisfactory method

as it overcomes difficulties, which are encountered in conventional methods of conductivity measurement *(i.e.*, two probes), *e.g* the rectifying nature of metal-semiconductor contacts and the injection of minority carriers by one of the current carrying contacts, which affects the potential of other contacts and modulate the conductance of the material *etc.* It also permits, measurement of conductivity in samples having wide variety of shapes. In order to use the four-probe method it is necessary to make the following assumptions:

- The conductivity of the material is uniform within the area of measurements. If there is minority carrier injection into the material to be tested by the current carrying electrodes, most of the carriers recombine near the electrodes so that their effect on the conductivity is negligible.
- The surface on which the probe rest is flat with no surface leakage.
- The four-probe used for conducting measurement must contact the surface at points that lie in a straight line.
- The diameter of the contact between the metallic probes and the material should be smaller than the distance between the probes.
- The surfaces of the materials may be either conducting or non-conducting.
- A conducting boundary is one in which the bottom surface of the material to be tested is of much higher conductivity than that of the material itself. This could be achieved by copper plating on the bottom surface of the semiconductor slice.
- A non-conducting boundary is produced when the bottom surface of the material to be tested is in contact with an insulator such as poly tetrafluoroethylene in these measurements.

After the measurements of current-voltage data by a 4-in-line probe dc electrical conductivity-measuring instrument was processed for calculation of resistivity (ρ_o) using the following equation-

$$\rho_o = (V/I) \times 2\pi S \quad \ldots\ldots 4.7$$

where *V* is the voltage (V) and *I* is the current (A).

Since the thickness of the sample is small compared to the probe distance a correction factor for it has to be applied and the corrected resistivity may be calculated as-

$$\rho = \rho_o/G_7(W/S) \quad \ldots\ldots 4.8$$

where ρ is the corrected resistivity in ohm. cm., $G_7(W/S)$ is the correction factor used in the case of non-conducting bottom surface and it is a function of *W*, thickness of the sample under test (cm) and *S*, probe spacing (cm); *i.e.*,

$$G_7(W/S) = (2S/W)\log_e 2 \quad \ldots\ldots 4.9$$

Thus, the electrical conductivity (σ) was calculated using the following equation-

$$\sigma = 1/\rho \quad \ldots\ldots 4.10$$

where σ is the electrical conductivity in Scm^{-1}.

Although the electrical conductivity measurements were done in the ambient conditions, the composite samples were thoroughly dried before making pellets and electrical conductivity measurements. So the contribution of protonic conductivity in total electrical conductivity due to the presence of moisture may be minimal and may not be taken into consideration.

The variations of electrical conductivity (σ) of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite samples (as prepared and HCl treated),

prepared with 33.33% pyrrole (PT-10) and 10% aniline (PS-5) concentrations (vol.%); respectively, with increasing temperature (between 30 °C to 140 °C) were carried out. On examination, it was observed that the electrical conductivity of the composite samples increase with the increase in temperature and the values lie in the order of 10^{-6} to 10^{-4} S cm^{-1} for polypyrrole Th(IV) phosphate and 10^{-5}-10^{-3} S cm^{-1} for polyaniline Sn(IV) phosphate *i.e.,* in the semiconductor region. To determine the nature of dependence of electrical conductivity on temperature plots of log σ versus 10^3T^{-1} K^{-1} were drawn (Fig. 4.1 and Fig. 4.2) and they followed Arrhenius equation similar to other semiconductors [38]. It was also observed that the composite materials showed enhanced electrical conductivity on exposure to HCl as compared to original form, due to the charge-transfer reaction between polypyrrole or polyaniline component of the composites and doping agents, HCl as described above.

The effect on electrical conductivity of the different forms (Na^+, Li^+, Ca^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}) of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers were also examined and presented in Table 4.3. It was observed that the electrical conductivity of both the composites was affected negligibly, when treated with the metal nitrate solutions of (Li^+, Na^+, K^+, Ca^{2+}), while the electrical conductivity of Pb^{2+}, Cu^{2+}, Mn^{2+}, forms of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate were decreased to 10^{-8}, beyond the semi-conducting region (Table 4.3).

The dependence of the electrical conductivity through the bi-phasic systems (polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composites; prepared with different concentrations of pyrrole and aniline monomers) on the

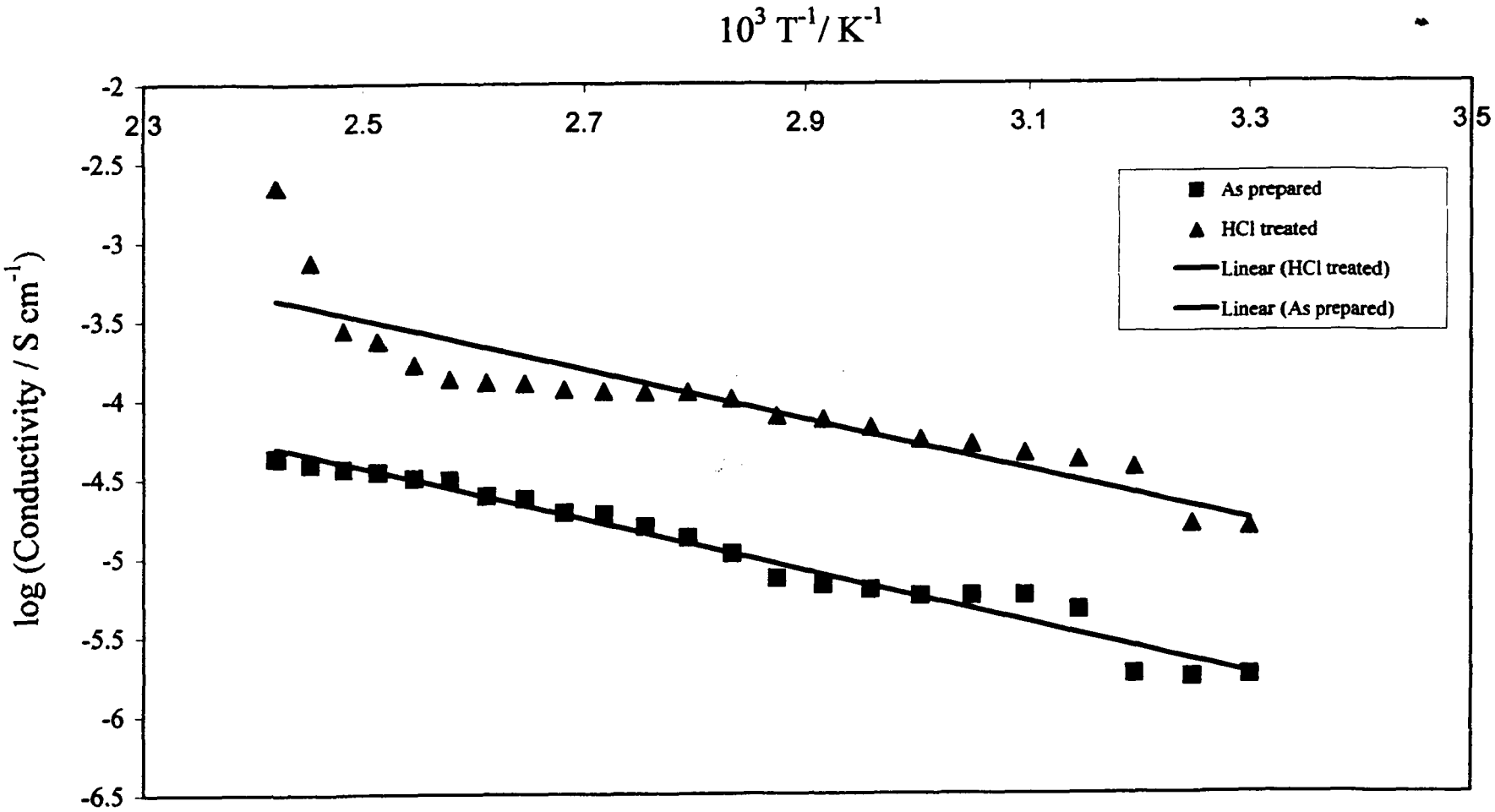

Fig. 4.1. Arrhenius plots for polypyrrole Th(IV) phosphate composite material (as prepared and HCl treated).

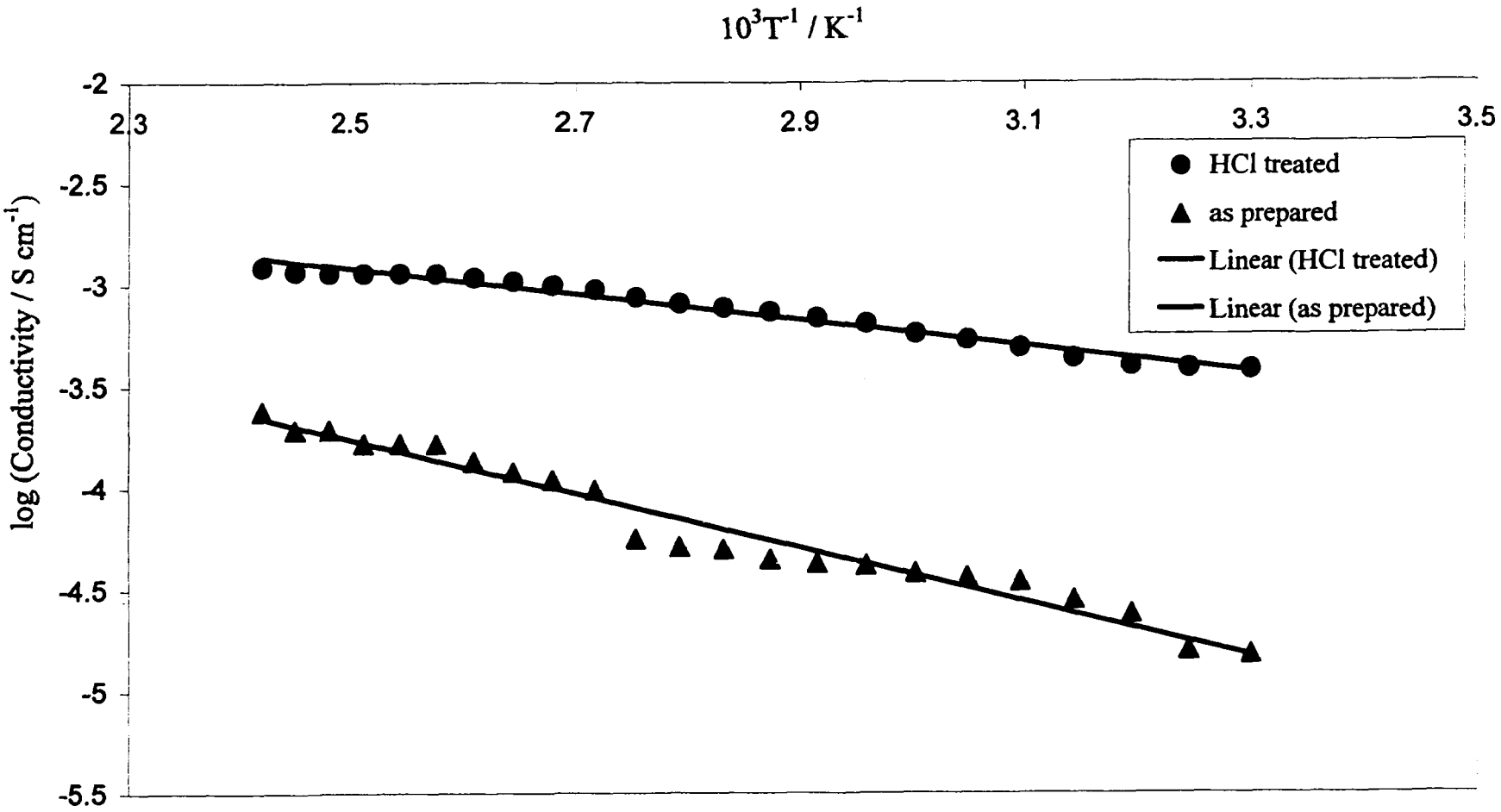

Fig.4.2. Arrhenius plots for polyaniline Sn(IV) phosphate composite material (as prepared and HCl treated).

Table 4.3

Four-probe dc electrical conductivity of different forms of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite systems at ambient temperature (prepared with 33.33% pyrrole and 10% aniline monomers, respectively)

Sample No.	Sample treatment	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)	
		Polypyrrole Th(IV) phosphate	Polyaniline Sn(IV) phosphate
1	As prepared	1.68×10^{-6}	2.39×10^{-4}
2	HCl treated	1.46×10^{-5}	5.85×10^{-3}
3	NaCl treated	2.27×10^{-4}	3.32×10^{-5}
4	KCl treated	1.25×10^{-5}	2.21×10^{-5}
5	LiCl treated	1.84×10^{-5}	1.41×10^{-5}
6	$CaCl_2$ treated	1.74×10^{-5}	1.06×10^{-5}
7	$Pb(NO_3)_2$ treated	2.04×10^{-8}	4.82×10^{-8}
8	$MnCl_2$ treated	1.26×10^{-8}	3.24×10^{-8}
9	$Cu(NO_3)_2$ treated	2.02×10^{-8}	6.24×10^{-8}

concentration of conducting phases (i.e. polypyrrole and polyaniline, respectively) was examined (Table 4.4 and 4.5). A slight increase in electrical conductivity for these composites is followed at a certain pyrrole and aniline concentration by a sudden jump, which is again followed by moderate increase. At about 23.33% pyrrole and 8% aniline concentration (critical concentration of conducting phase), the sharp rise in electrical conductivity is observed that could possibly be explained on the basis of percolation theory [39]. Thus, we can say that main factor that made the composites electrically conductive is the presence of polypyrrole or polyaniline in sufficient amount. Thus, major part of electrical conductivity of the composite is due to the incorporation of polypyrrole or polyaniline in the composites.

It was also observed that the ambient temperature conductivities of the composites for some concentrations of pyrrole and aniline monomers are greater than that of polypyrrole (prepared as 33.33% pyrrole in toluene) and polyaniline (prepared as 10% aniline in 1 M HCl) as shown in Table 4.4 and 4.5.

4.3.2. Stability of composites in terms of dc electrical conductivity retention

It is generally considered for the thermal degradation of the usual polymers that the elimination of hydrogen/loss of dopant from the polymer chains occurs at high temperatures, and an oxygen molecule reacts with the generated radicals in air. In case of polypyrrole and polyaniline, this would stop the extension of the π conjugation of polypyrrole and polyaniline chains. Therefore, decrease in electrically conductivity occurs. Thus, the factors that influence the stability of the conductivity

Table 4.4

Values of dc electrical conductivity for the polypyrrole and polypyrrole Th(IV) phosphate composites with different concentrations of pyrrole monomer

Sample No.	Polypyrrole (prepared with 33.33% pyrrole in toluene)	Polypyrrole Th(IV) phosphate	
	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)	Pyrrole monomer concentration (vol. %)	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)
1	3.28×10^{-5}	3.33	4.13×10^{-8}
2		6.66	5.19×10^{-8}
3		10	2.82×10^{-8}
4		13.33	3.84×10^{-8}
5		16.66	5.92×10^{-8}
6		20	6.15×10^{-8}
7		23.33	2.53×10^{-5}
8		26.66	3.47×10^{-5}
9		30	3.54×10^{-5}
10		33.33	3.82×10^{-4}
11		36.66	4.90×10^{-4}
12		40	5.16×10^{-4}

Table 4.5

Values of dc electrical conductivity for the polyaniline and polyaniline Sn(IV) phosphate composite with different concentrations of aniline monomer

Sample No.	Polyaniline (prepared with 10% aniline in 1 M HCl)	Polyaniline Sn(IV) phosphate	
	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)	Aniline monomer concentration (vol. %)	Ambient temperature dc electrical conductivity ($S\ cm^{-1}$)
1	9.12×10^{-4}	2	3.20×10^{-6}
2		4	5.82×10^{-6}
3		6	9.46×10^{-5}
4		8	2.54×10^{-4}
5		10	5.23×10^{-3}
6		12	6.48×10^{-3}
7		14	6.93×10^{-3}
8		16	8.01×10^{-3}
9		18	5.20×10^{-3}
10		20	3.12×10^{-3}

of composites are of considerable interest, both from fundamental and industrial perspectives. However, the stabilities of the composites were dependent on the preparation conditions employed.

The thermal stability of the polypyrrole Th(IV) phosphate (PT-10) and polyaniline (PS-5) composite materials (HCl treated) in terms of dc electrical conductivity retention was studied under isothermal condition (at 50, 70, 90, 110, 130 and 150 °C) measuring 4-in-line- probe dc electrical conductivity at an interval of 15 minutes. The electrical conductivity measured with respect to the time of accelerated ageing is presented in Fig. 4.3 and Fig. 4.4. It was observed that the electrical conductivity for both the composite materials is quite stable at 50, 70, 90 and 110 °C that supports the fact that the dc electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150 °C that may be attributed to the loss of dopant and the chemical reaction of dopant with the material. The stability of both HCl treated composite materials (PT-10 and PS-5) in terms of electrical conductivity retention was also monitored for 5 cycles by repeatedly measuring linear four-probe dc electrical conductivity with increase in temperature at an interval of 45 minutes and the dc conductivity for each heating cycle was plotted as log σ versus $10^3 T^{-1} K^{-1}$ as shown in Fig. 4.5 and 4.6. It was observed for both the composite materials that each plot followed the Arrhenius equation for its temperature dependence similar to other semiconductors [38]. There was minor difference in their electrical conductivity even after repeating the experiment for five times that showed the good stability of the material during heating-cooling cycles under severe oxidizing conditions upto 200 °C.

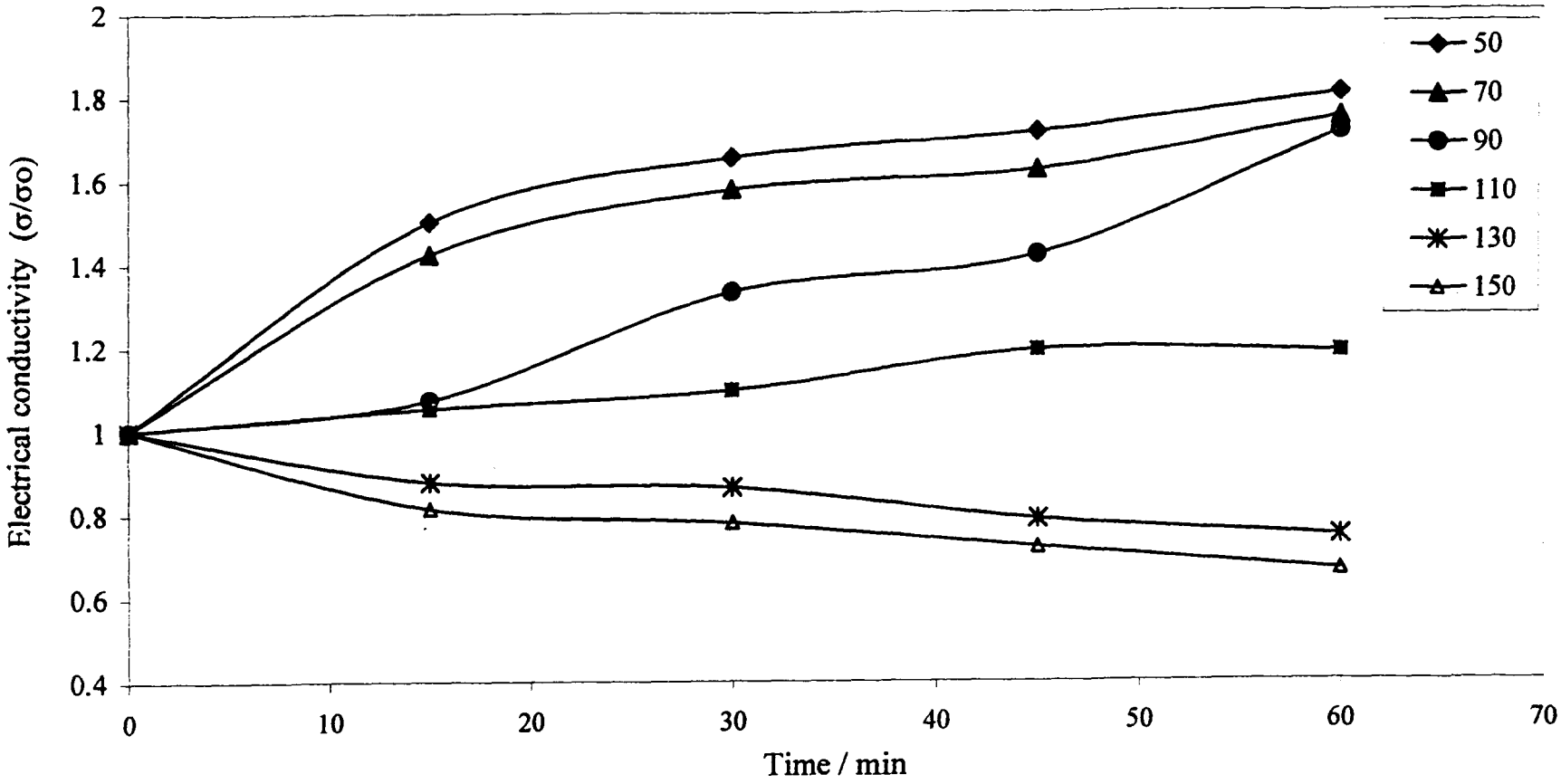

Fig. 4.3. Isothermal stability of polypyrrole Th(IV) phosphate composite (HCl treated) in terms of retention of dc electrical conductivity with respect to time at 50, 70, 90, 110, 130 and 150 °C.

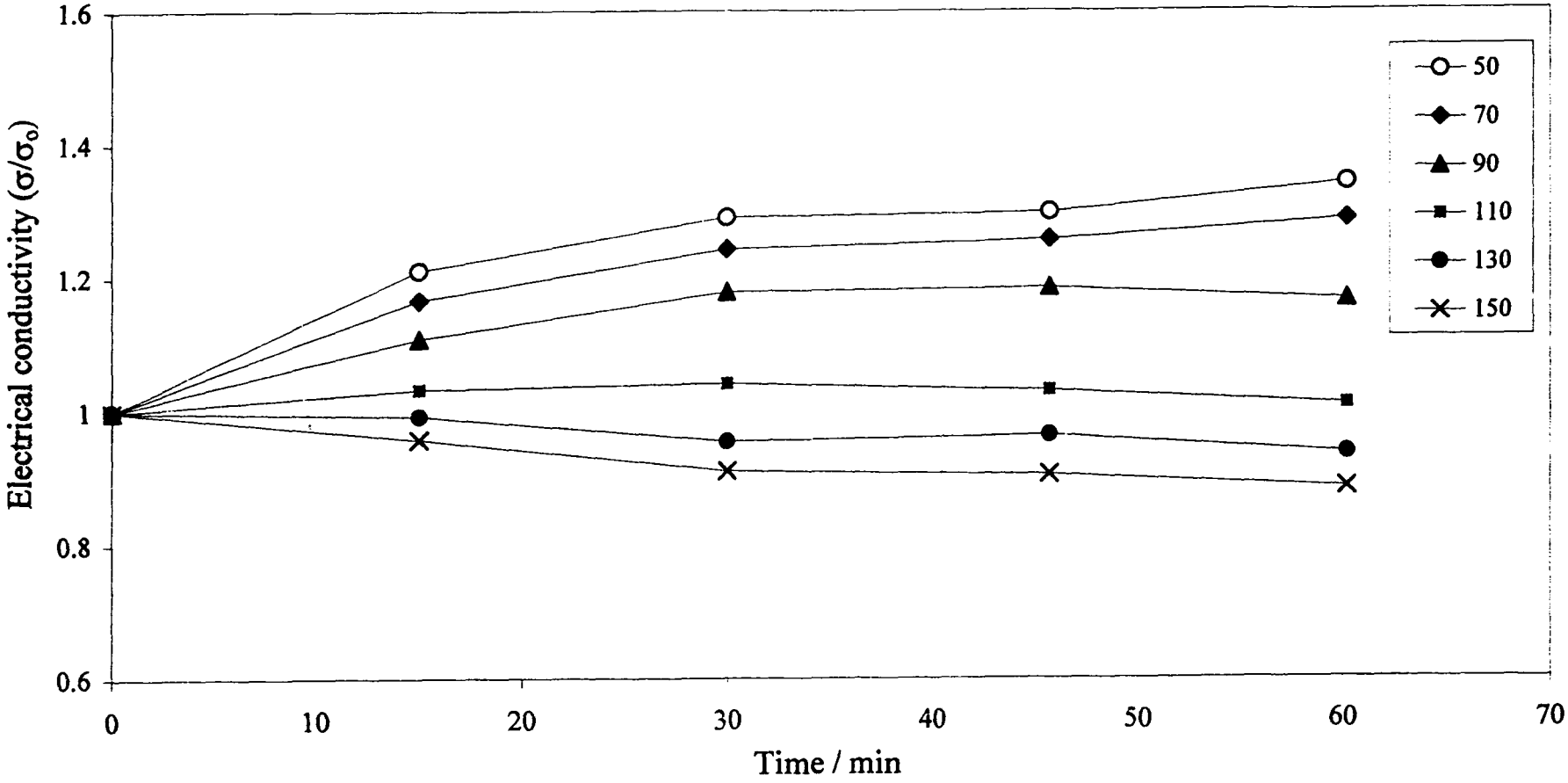

Fig. 4.4. Isothermal stability of polyaniline Sn(IV) phosphate composite (HCl treated) in terms of retention of dc electrical conductivity with respect to time at 50, 70, 90, 110, 130 and 150 °C.

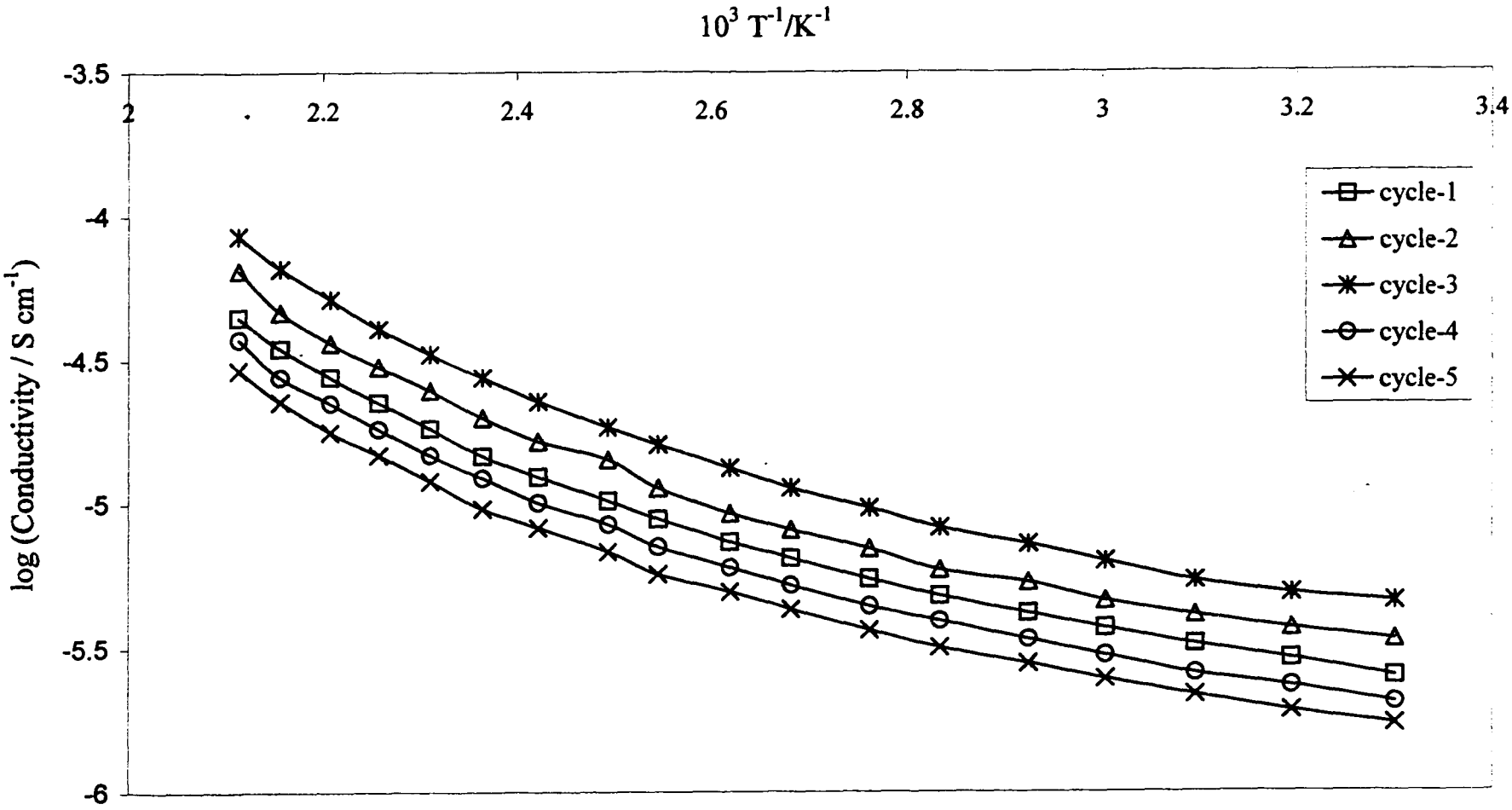

Fig. 4.5. Arrhenius plots of retention of dc electrical conductivity for polypyrrole Th(IV) phosphate composite (HCl treated) during heating-cooling cycles upto 200 °C.

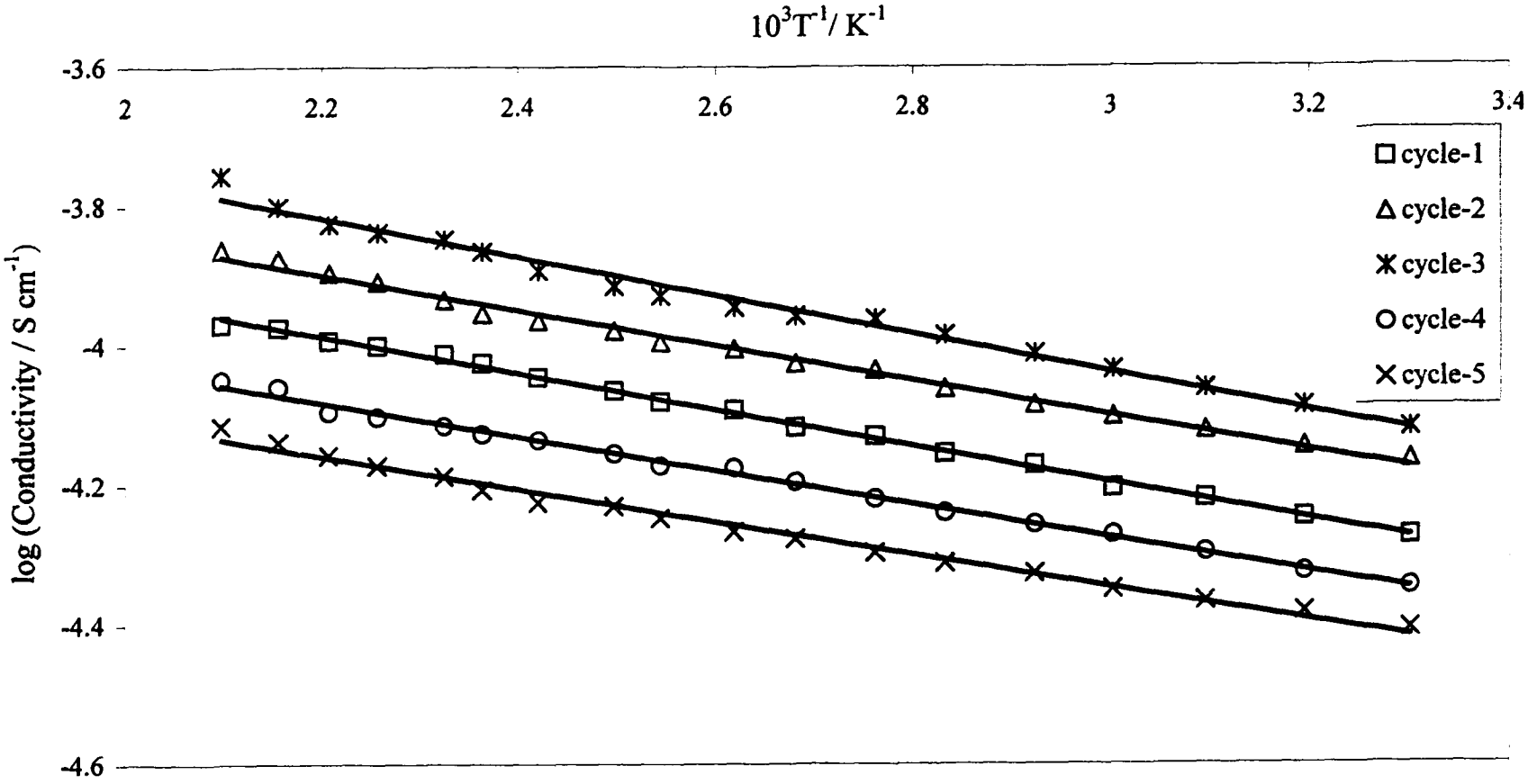

Fig. 4.6. Arrhenius plots of retention of dc electrical conductivity for polyaniline Sn(IV) phosphate (HCl treated) during heating cooling cycles upto 200 °C.

These composite materials were also observed to be a stable material, *i.e.*, the room temperature conductivity is negligibly affected by short-term exposure to laboratory air as evident from Fig. 4.7 and 4.8. The materials of these types may often exhibit an increase in conductivity upon short-term exposure to oxygen, which is attributed to the formation of a charge transfer complex with oxygen and may involve O^{2-}. Presumably, electron transfer from the polymer moiety to oxygen occurs, resulting in an increased extent of oxidation of the polymer chain. Thus short-term exposure to oxygen may increase the conductivity of the material by increasing the concentration of charge carriers. Oxygen can also produce a decrease in the conductivity of the material through a destructive reaction; *e.g.* exposure of the composite to oxygen results in a decrease in the conductivity due to an irreversible reaction that is believed to generate covalently bonded oxygen species. Axially bound water is also responsible for part of the conductivity loss during the ageing of the material.

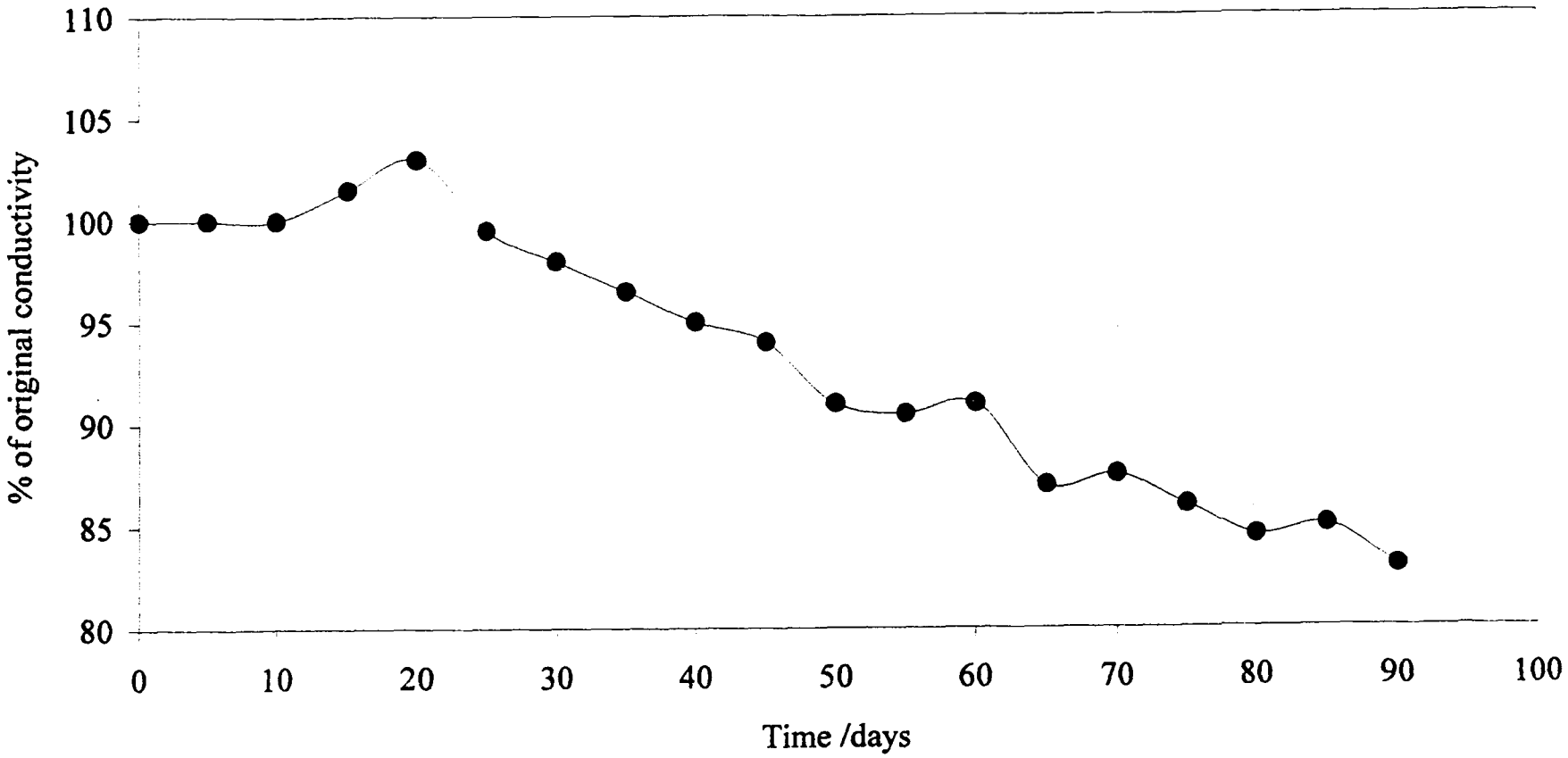

Fig. 4.7. Conductivity versus time of exposure to laboratory air for polypyrrole Th(IV) phosphate composite material (HCl treated).

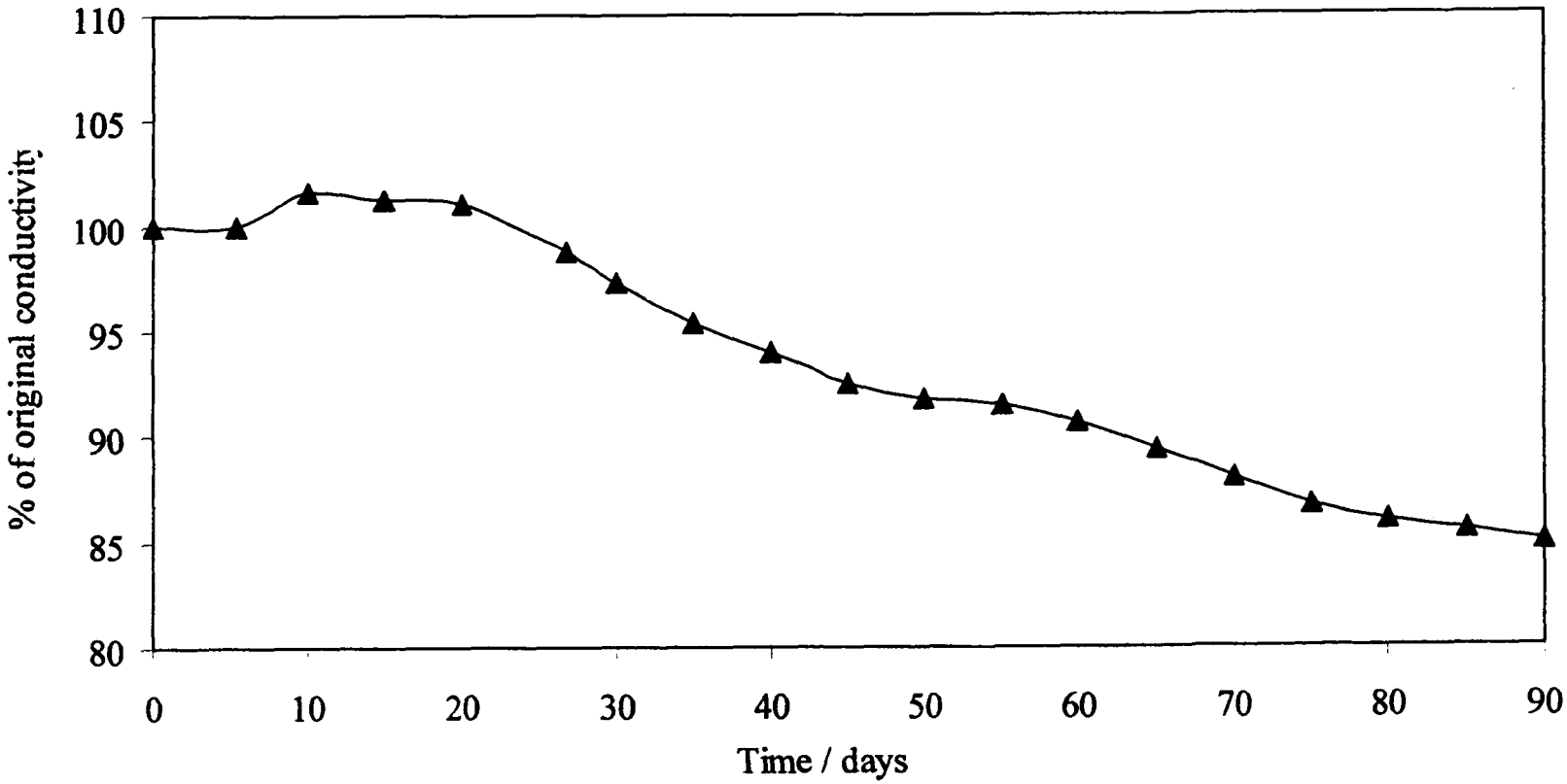

Fig. 4.8. Conductivity versus time of exposure to laboratory air for polyaniline Sn(IV) phosphate composite material (HCl treated).

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Chapter 5

Preparation and Characterization of Ion- Exchange Membranes and Ion-Selective Electrodes based on Polypyrrole Th(IV) phosphate and Polyaniline Sn(IV) phosphate

Chapter 5

5.1. Introduction

The increasing demand for chemical surveillance in environmental protection, medicine and many industrial processes has created the need for sensors with features such as high selectivity, sensitivity, reliability and sturdiness. These demand can often be satisfied by ion-selective electrodes (ISEs), which are commonly used owing to their simplicity, lower cost, fast provision for analytical results and high selectivity for heavy toxic metal ions [1,2]. Therefore, ion-selective electrodes are important analytical tools allowing the sensitive and selective determination of great number of ions in the wide range of concentration [3]. Thus, over the past decades ion-selective electrode based potentiometry has become a well-established electroanalytical technique. In this technique the most exciting and fastest growing area of research is the use of ion sensitive membrane electrodes for analysis of wastewater containing heavy metals. Using this approach the applicability of the potentiometric method has been greatly extended enabling the simple and accurate determinations of many heavy metal ions and has led to a search for suitable materials that can be used for preparation of sensitive and selective ion-sensors, chemical sensors or more commonly ion-selective electrodes (ISEs). Precipitate based ion-selective membrane electrodes are well known as they are successfully employed for the determination of several anions and cations [4-15]. There are some homogeneous as well as heterogeneous hybrid ion-exchange membranes. Homogeneous ion-exchange

membranes are coherent ion-exchanger gels in the shape of disks, ribbons, etc. The heterogeneous precipitate ion-exchange membranes consisting of suitable colloidal ion-exchanger particles as electroactive materials embedded in a polymer (inert) binder, i.e., poly(vinyl chloride) (PVC), or epoxy resin (Araldite), or polystyrene, polyethylene, nylon, PMMA, etc., have been extensively studied as potentiometric sensors [16-27]. Ion-exchange membranes also find application in diverse processes such as (electro-dialysis, diffusion dialysis, electro-deionization, membrane electrolysis, fuel cells, storage batteries, electro-chemical synthesis *etc.*), which are energy resource and environmental saving. Thus, the development of ion-exchange membranes of high chemical, mechanical, and thermal stabilities, which meet the growing demand of the previously mentioned processes, is of great importance.

Now a days, the use of 'organic-inorganic' composite ion-exchange materials formed by the combination of inorganic precipitates and organic polymers as electroactive components in membrane electrodes has generated widespread interest in developing new ion-selective electrodes (ISEs) for sensor applications [28-32], especially for the determination of heavy toxic metals [33-35].

Metal toxicity to humans has become a great challenge. Among many toxic metals, lead is one which poses a serious health threat, if present in concentrations exceeding the permissible limits. Lead in the environment arises from both natural and anthropogenic sources. Generally, human exposure to lead comes from the following main sources: using leaded gasoline; using lead-based paint; having lead pipes in water supply systems; and exposure to industrial sources from processes such as lead mining, smelting, and coal combustion. Additional sources of lead

include soldered seams in food cans, ceramic glazes, batteries, and cosmetics [36]. In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. Particularly, lead is toxic to the brain, kidneys, reproductive system, and cardiovascular system. Exposures can cause impairments in intellectual functioning, kidney damage, infertility, miscarriage, and hypertension [37]. Lead is a special hazard for young children. Lead exposures have also been associated with aggressive behavior, delinquency, and attention disorders in boys between the ages of 7 and 11 [38]. In adults, lead exposure has been related to increased blood pressure and hypertension, conditions known to increase the risk of cardiovascular disease. Because ion-selective electrodes provide rapid, accurate and low cost analysis attempt have been made during the last few decades to develop ion-selective electrodes for the selective determination of lead [39-48], a toxic metal of the environment. Recently, composite materials are well known as useful materials for the fabrication of lead ion-selective electrodes of various electrometric sensors for analytical purposes [49].

Mercury is a toxic persistent bioaccumulative pollutant that affects the nervous system. It is found as industrial waste because of its growing area in production of some batteries, thermometers, cameras, cathode tubes, calculators, medical laboratory chemicals, a catalyst in production of urethane polymers for plastics, a cathode in electronic production of chlorine and caustic soda, mercury vapor lamps and barometers. Methyl mercury is a chemical species that

bioaccumulate in fish. Fish consumption advisories are in effects for mercury in thousands of lakes and rivers, including much of the Great lakes ecosystem.

The harmful effects of mercury may cause cancer, damages of the stomach, large intestine and lungs, and can also increase blood pressure and heart rate. Thus, it is very important to determine mercury at lower and lower levels in our environments. Although various common methods are used to determine mercury such as voltametry [50], spectrophotometry [51,52], X-ray fluorescence [53], flame and furnace atomic absorption spectrometry [54,55] fluorimetry [56,57], cold vapor atomic absorption spectrometry [58] and inductively coupled plasma [59]. Recently, composite materials are well known and used for the fabrication of various electrometric sensors for analytical purposes [33,34,35,60-62].

Therefore, we have also made an effort to develop composite cation-exchangers through incorporation of electrically conducting organic polymers *i.e.* polypyrrole and polyaniline into the matrices of inorganic precipitates of multivalent metal acid salts *i.e.* Th(IV) phosphate and Sn(IV) phosphate, respectively that are attractive for the purpose of creating high performance or high functional polymeric materials with good electrochemical properties. Since the newly developed polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers are highly selective for Pb(II) and Hg(II) ions; (as shown in Chapter-3, Section 3.2.4.6), the further research work was carried out to obtain new heterogeneous precipitate based membrane ion-selective electrodes by means of these composites as electroactive phase for the determination of Pb(II) and Hg(II) ions; present in the solutions. This chapter represents the preparation, characterization and fabrication of ion-exchanger membranes and ion-selective membrane electrodes based on the aforesaid composite materials.

5.2. Experimental

5.2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical reagent grade.

The stock solution of 1×10^{-1} M Pb(II) and Hg(II) were prepared by dissolving 3.3121 g of $Pb(NO_3)_2$ and 3.4262 g of $Hg(NO_3)_2$ in 100 ml of DMW, respectively. The solutions were standardized by complexometric titration [63]. The working standard of Pb(II) and Hg(II) solutions (1×10^{-1} to 1×10^{-9} M) were prepared by proper dilution of both stock solutions.

A digital pH-meter (Elico LI-10, India), a digital potentiometer (Equiptronics EQ 609, India; accuracy ± 0.1 *mV*) with a saturated calomel electrode as a reference electrode, an electronic balance (digital) – (Sartorius 21 OS, Japan) and an agate mortar pastel were used.

5.2.2. Preparation of electroactive phases: polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-Exchangers

A number of samples of 'polypyrrole Th(IV) phosphate' and polyaniline Sn(IV) phosphate composite cation-exchange materials were prepared as described in Chapter – 2 (Section 2.2.3.). But the sample S-5 (Table 2.1) and sample T-7 (Table 2.2) were chosen as electroactive phase for the potentiometric studies.

5.2.3. Preparation of ion-exchange membranes

The ion-exchange membranes were prepared by employing an electroactive ion-exchange material into a polymer binder. For this purpose, electroactive component polypyrrole Th(IV) phosphate (S-5) composite cation-exchange material was taken to be embedded in Araldite (an epoxy resin), while polyaniline Sn(IV) phosphate (T-7) was embedded with polyvinyl chloride (PVC).

5.2.3.1. Preparation of polypyrrole Th(IV) phosphate membrane

The ion-exchange membranes were prepared by following the procedure of *Coetzee* and *Benson* [19]. Polypyrrole Th(IV) phosphate cation-exchanger (100 mg) as electroactive material was grinded to fine powder, and was mixed thoroughly with Araldite (Ciba-Geigy, India Ltd.) (100 mg) in 1:1 (*w/w*) ratio to make a homogeneous paste, which was, then spread between the folds of Whatman's filter paper No. 42. Glass plates were kept below and above the filter paper folds as support. The phase of the exchanger and Araldite was kept under pressure of 2 Kg. cm^2 for 24 h and left to dry. Three sheets of different thickness 0.42, 0.50, 0.55, mm of master membranes were prepared. These sheets were dipped in distilled water to remove filter paper. After drying, the membrane sheets were cut in the shapes of discs using a sharp edge blade.

5.2.3.2. Preparation of polyaniline Sn(IV) phosphate membrane

The electroactive material *i.e.* polyaniline Sn(IV) phosphate cation-exchanger was grinded to fine powder, and was mixed thoroughly with polyvinyl chloride

(PVC), dissolved in 10 ml of tetrahydrofuran (THF) and finally mixed with 10 drops of dioctylphthalate used as plastisizer [64]. The mixing ratio of the ion-exchanger was varied with a fixed content of PVC in order to obtain a composition, which gave the membrane showing the best performance and the resulting solutions were carefully poured into a glass-casting ring (diameter 10 mm) resting on a glass plate. These rings were left for slow evaporation of THF to obtain thin films. In this way four sheets of different thickness 0.36, 0.46, 0.56, 0.78 mm of master membranes were obtained.

5.2.4. Characterization of membranes

The pre-requisite performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters were membrane water content, porosity, thickness, swelling, *etc.* and were determined as described elsewhere [65-68] after conditioning the membrane as given below.

5.2.4.1. Conditioning of the membrane

The membranes were conditioned by equilibrating with 1 M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH 5-6.5 (to neutralize the acid present in the film).

5.2.4.2. Water content (% total wet weight)

The conditioned membranes were first soaked in water to elute diffusible salts, blotted quickly with Whatman filter paper to remove surface moisture, and

immediately weighed. These were further dried to a constant weight in a vacuum over P_2O_5 for 24 h. The water content (% total wet weight) was calculated as:

$$\%\ Total\ wet\ weight = \frac{W_w - W_d}{W_w} \times 100$$

where W_w = weight of the soaked/wet membrane and W_d = weight of the dry membrane.

5.2.4.3. Porosity

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data.

$$\varepsilon = \frac{W_w - W_d}{AL\rho_w}$$

where W_w = weight of the soaked/wet membrane, W_d = weight of the dry membrane, A = area of the membrane, L = thickness of the membrane and ρ_w = density of water.

5.2.4.4. Thickness and Swelling

The thicknesses of the membranes were measured by taking the average thickness of the membrane by using screw gauze.

Swelling was measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane.

5.2.5. Fabrication of ion-selective membrane electrode

The membrane sheets of polypyrrole Th(IV) phosphate (0.42 mm thickness) and polyanilne Sn(IV) phosphate (0.36 mm thickness) as obtained by the above

procedures were cut in the shape of disc and mounted at the lower end of a pyrex glass tube (o.d. 0.8 cm, i.d. 0.6 cm) with Araldite. Finally the assembly was allowed to dry in air for 24 h. The glass tube was filled with solution of the ion (as internal reference) towards which the membrane is selective and kept dipped in an identical solution of the same ion at room temperature. In case of polypyrrole Th(IV) phosphate ion-selective membrane electrode, the glass tube was filled with 0.1 M lead nitrate, $Pb(NO_3)_2$ solution, while for polyaniline Sn(IV) phosphate filled with a 0.1 M mercuric nitrate, $Hg(NO_3)_2$ solution. Saturated calomel electrodes were inserted into both the tube for electrical contact and another saturated calomel electrodes were used as an external reference electrode. The whole arrangement for both the ion-selective membrane electrodes can be shown as:

Internal reference electrode(SCE) Hg, Hg_2Cl_2(s) KCl (satd.)	Internal electrolyte (0.1 M Pb^{2+})	Membrane	Sample solution	External reference electrode (SCE) Hg, Hg_2Cl_2(s) KCl (satd.)

and

Internal reference electrode(SCE) Hg, Hg_2Cl_2(s) KCl (satd.)	Internal electrolyte (0.1 M Hg^{2+})	Membrane	Sample solution	External reference electrode (SCE) Hg, Hg_2Cl_2(s) KCl (satd.)

5.2.6. Characterization of ion-selective membrane electrodes

In order to study the characteristics of both the electrodes, the following parameters were evaluated: lower detection limit, electrode response curve, response time, working pH range and selectivity.

5.2.6.1. Electrode response or membrane potential

The potentiometric measurements of the membrane electrodes were carried out by setting up a cell of the above type. To determine the electrode response, a series of standard solutions to be studied of varying concentrations were prepared. External electrode and ion-selective membrane electrode are plugged in digital potentiometer and the potentials were recorded.

The response of both the electrodes in terms of the electrode potential (at 25 ± 2 °C), corresponding to the concentration of a series of standard solutions of $Pb(NO_3)_2$ and $Hg(NO_3)_2$ in the range ($1 \times 10^{-9} - 1 \times 10^{-1}$ M), were determined at a constant ionic strength as described by IUPAC Commission for Analytical Nomenclature [69]. A calibration curve was made by measuring the electrode response to standard solutions prepared by serial dilution without the addition of extra indifferent salts. The ionic strength will increased linearly with an increase in concentration. This will lead to a gradual decrease of the activity coefficient, and the calibration curve [E versus log(concentration)] showed a negative deviation from the straight line for concentrations above 10^{-3} to 10^{-2} M. This curvature of the calibration curve can be precluded by working at constant ionic strength. This is commonly achieved by adding a large excess of an indifferent electrolyte, the ionic strength buffer.

The membrane electrodes were conditioned by soaking:

- in 0.1 M $Pb(NO_3)_2$ solution for 5-7 days and for 1 hour at least before use for the polypyrrole Th(IV) phosphate membrane electrode.

- in 0.1 M $Hg(NO_3)_2$ solution for 5 days and for 1 h at least before use for the polyaniline Sn(IV) phosphate ion-selective membrane electrode.

The experiments were conducted in air thermostat maintained at 25 ± 1 °C, after performing the experiments membrane electrodes were removed from the test solution and kept in a 0.1 M selective metal ion solution. Potential measurements of the membrane electrode were plotted against the selected concentrations of the respective ions in aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system.

5.2.6.2. Response time

The response time was measured by recording the e.m.f. of both the electrodes as a function of time when it was immersed in the solution to be studied. The method of determining response time in the present work is being outlined as follows:

The electrode was usually first dipped in a 1×10^{-3} M solution of the ion concerned and immediately shifted to another solution (pH ≈ 4.0) of 1×10^{-2} M ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second, that is, just after immediate dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 s (Table 5.1). The potentials were then plotted against the time. The time during which the potentials attain a constant value represents the response time of the electrode.

Table 5.1

Response of Pb^{2+} ion-selective polypyrrole Th(IV) phosphate and Hg^{2+} ion-selective polyaniline Sn(IV) phosphate membrane electrodes at different time interval

Time (Sec.) ⇓ Membranc electrodes ⇒	Measured electrode potential (- mV)	
	Polypyrrole Th(IV) phosphate	Polyaniline Sn(IV) phosphate
00	1000	990
05	970	981
10	950	965
15	920	945
20	910	925
25	895	910
30	880	893
35	870	877
40	870	861
45	880	860
50	870	860
55	870	860
60		860

5.2.6.3. Effect of pH

A series of solutions of varying pH for polypyrrole Th(IV) phosphate (in the range of pH 1 to 13) and polyaniline Sn(IV) phosphate (in the range of pH 1 to 14) were prepared, keeping the concentration of the relevant ion constant (1×10^{-3} M) for the electrodes. The pH variations were brought out by the addition of dilute acid (HCl) or dilute alkali (NaOH) solutions. The values of electrode potential for both the electrodes at each pH were recorded (Table 5.2) and were plotted against pH.

5.2.6.4. Selectivity coefficients

To study the cationic interference due to other ions, the selectivity coefficients of various interfering cations for the polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate ion-selective membrane electrodes were determined by the mixed solution method as discussed elsewhere [70]. The method is discussed below.

A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-3} M) and varying concentrations (1×10^{-1} to 1×10^{-9} M) of the primary ion. Now the potential measurements were made by using the membrane electrode assembly.

5.2.5.5. Life span of membrane electrode

In order to find out the lifetime of the electrode, the electrode responses were noted every week and response curve is drawn for the data. The electrode response remains fairly constant over a period of time. After this period the electrode starts behaving irregular, therefore cannot be used for any measurements. This period over which the electrode response is constant can be termed as life of electrode.

Table 5.2

Effect of pH on electrode response of Pb^{2+} ion-selective polypyrrole Th(IV) phosphate and Hg^{2+} ion-selective polyaniline Sn(IV) phosphate membrane electrodes

pH ⇓ Membrane electrodes ⇒	Measured electrode potential (- mV)	
	Polypyrrole Th(IV) phosphate	Polyaniline Sn(IV) phosphate
1	800	967
2	845	935
3	900	892
4	899	870
5	898	869
6	902	868
7	900	868
8	901	867
9	920	868
10	945	886
11	970	901
12	995	919
13	1012	939
14		953

5.3. Results and Discussions

In this chapter, electrically conducting 'organic-inorganic' composite cation-exchangers 'polypyrrole Th(IV) phosphate' and 'polyaniline Sn(IV) phosphate' were used as an electroactive material embedded in inert polymer binder Araldite (an epoxy resin) and PVC respectively, for the preparation of heterogeneous ion-selective membrane electrode. These inert polymer binders are found to be effective matrix materials for providing membranes of liquid ion-exchangers and carrier complexes for use in ion-selective membrane electrodes. They provide sufficient mechanical strength for the membranes to be used in electrodes without a strengthening support. They are simple and economical to use while their ranges of applications are typical of ion-selective electrodes and extend to the direct determination of activity with the aid of calibration graphs, continuous monitoring and potentiometric titrations.

5.3.1. Characterization of composite cation-exchanger membranes

It is well known that the sensitivity and selectivity of the ion-selective electrodes depend not only on the nature of electroactive material used, but also significantly on the membrane composition and the physico-chemical properties of the membranes employed. A number of samples for the polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate membranes were prepared with fixed amounts of Araldite and PVC and checked for the mechanical stability, surface uniformity, material distribution, cracks and thickness, *etc.* All the membranes

were found to be good, and showed the best mechanical stability as well as electro-chemical performance.

Characterization of the sensor membrane is essential to correlate with the movement of ions in the membrane phase, potential generated across it and the selectivity of ions of interest. So, it is necessary to have a preliminary investigation with the membrane that must exhibit some promising selectivity for particular metal ions. Thus, the thickness, swelling, porosity and water content capacity, *etc.*, of the polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate cation-exchanger membranes were investigated, to find out one membrane of good electrochemical performance for the purpose of preparation of ion-selective membrane electrode and the results are summarized in Table 5.3 and Table 5.4. When a membrane is immersed in a salt solution, swelling takes place and the solution penetrates into the membrane structure. The swelling should also be small for a membrane to exhibit good electrochemical performance. The membrane sample M-1 (thickness 0.42 mm) for polypyrrole Th(IV) phosphate and sample M-1 (thickness 0.36 mm) for polyaniline Sn(IV) phosphate were selected for further studies. Thus, the low order of water content, swelling and porosity with less thickness of these membranes suggest that interstices are negligible and diffusion across the membranes would occur mainly through the exchange sites.

Table 5.3

Characterization of polypyrrole Th(IV) phosphate ion-exchanger membranes

Polypyrrole Th(IV) phosphate membranes	Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
M-1	0.42	4.88	0.064	0.2
M-2	0.50	5.61	0.094	0.2
M-3	0.55	7.87	0.112	0.2

Table 5.4

Characterization of polyaniline Sn(IV) phosphate ion-exchanger membranes

S. No.	Membrane composition			Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
	Polyaniline Sn(IV) phosphate (mg)	PVC (mg)	Plasticizer (drops)				
S-1	100	200	10	0.36	2.25	0.074	0.2
S-2	150	200	10	0.46	3.29	0.101	0.2
S-3	200	200	10	0.56	15.73	0.321	0.2
S-4	250	200	10	0.78	16.63	0.573	0.2

5.3.2. Potentiometric studies of heterogeneous polypyrrole Th(IV) phosphate membrane electrode

The membrane (sample M-1) under investigation prepared from polypyrrole Th(IV) phosphate composite cation-exchange material was fabricated into ion-selective electrode and the membrane electrode was placed in 0.1 M $Pb(NO_3)_2$ solution for 7 days to get it conditioned. The choice of Pb^{2+} ions depends on its distribution behavior pattern.

After conditioning of the electrode, the potentials for a series of standard solution of the lead nitrate in the range 10^{-9} M – 10^{-1} M were measured, maintaining a fixed concentration of Pb^{2+} ion as internal reference solution. It was observed that the most favorable concentration of reference solution, for smooth functioning of the proposed membrane sensor is 0.1 M.

Potential measurement of the heterogeneous precipitate based membrane electrode was plotted against the selected concentrations of the Pb^{2+} ions (Fig. 5.1) and gave linear response, as shown in Figure 5.1, for the Pb(II) ions in the concentration range of 1×10^{-1} to 5×10^{-6} molar. Suitable concentration was chosen corresponding to the sloping portion of the linear curve. The slope of this linear curve is important and tells whether the electrode response follows the Nernstian response or not. The limit of detection was determined from the intersection of the two extrapolated segments of the calibration graph [71] and was found to be 5×10^{-6} molar. Thus, the working concentration range was found to be 1×10^{-1} to 5×10^{-6} M for Pb^{2+} ions with an average slope of 29.17 mV per decade change in Pb(II) ion

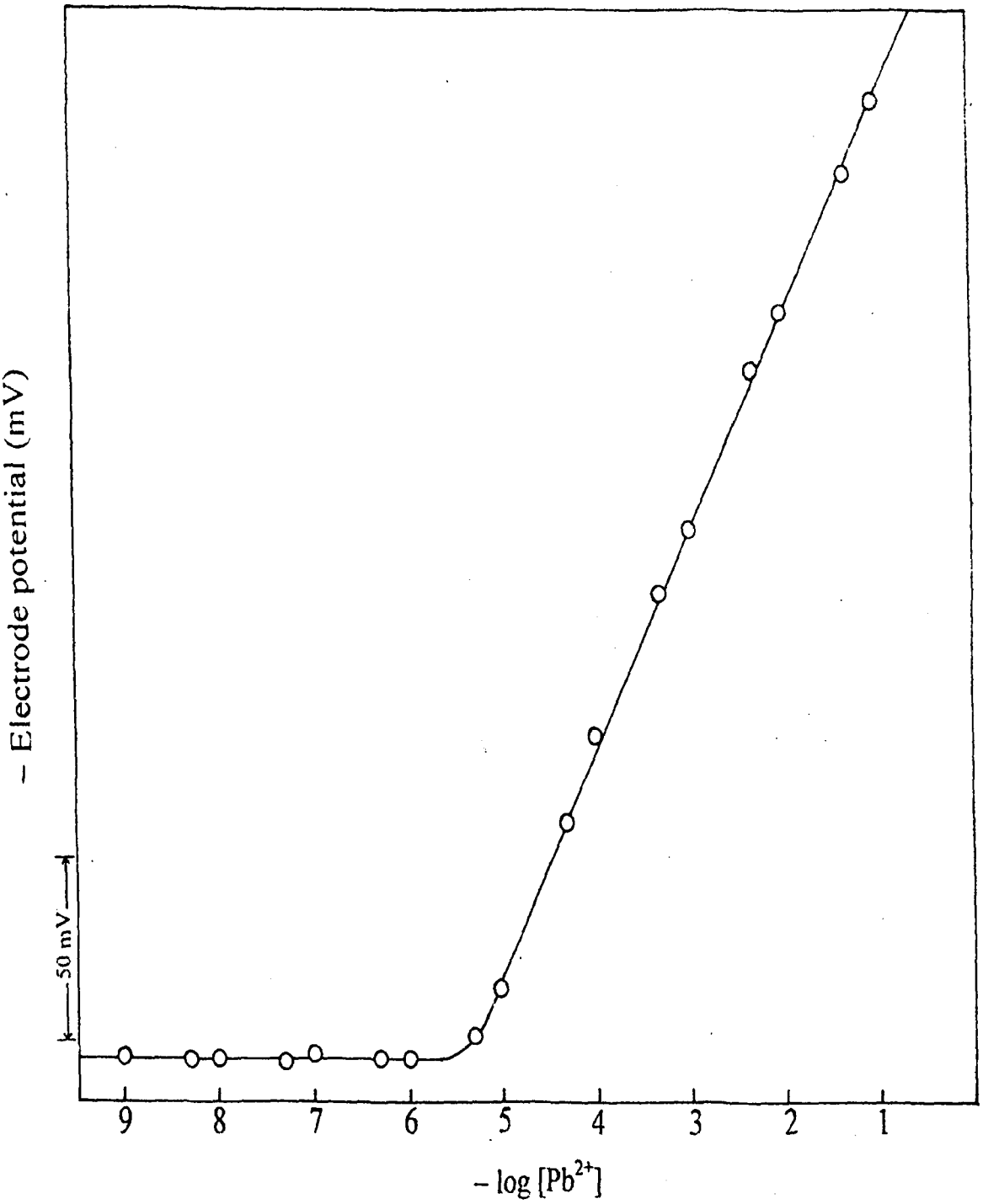

Fig. 5.1. Calibration curve for polypyrrole Th(IV) phosphate membrane electrode in aqueous solution of $Pb(NO_3)_2$.

concentration. The slope value is close to Nerstian value, 29.6 mV per concentration decade for divalent cations. Below 5×10^{-6} M, a non-linear response was observed but the calibration curve could be utilized for the determination of lead down to 5×10^{-6} M. It is stated in the literature that the electrodes with slopes in that vicinity range value could be used for analytical applications [72].

Another important factor besides linear response that commends the use of ISEs or membrane electrode is the promptness of the response of the electrode. The average response time is defined [73] as the time required for the electrode to reach a stable potential within ±1 mV of the final equilibrium value, after successive immersion of the electrode in different Pb^{2+} solutions each having a 10-fold difference in concentration. However, the interpretation of response time varies from a group of workers to others. *Pungor et al* [74-76] have discussed this aspect in details.

The response time in contact with 1.0×10^{-2} M Pb^{2+} ion solution was determined (Table 5.1) for the membrane electrode and the results are shown in Fig. 5.2. It is observed that the static response time of the membrane sensor is found to be ~ 35 s.

In order to investigate the pH effect on the potential response of the electrode, the potentials were measured for a fixed concentration of Pb^{2+} ions having different pH values. These measurements were carried out at different concentrations (1.0×10^{-2} M and 1.0×10^{-3} M) of Pb^{2+} ions but the results (values of electrode potential at each pH) only for 1.0×10^{-2} M Pb^{2+} ion solutions were recorded (Table 5.2).

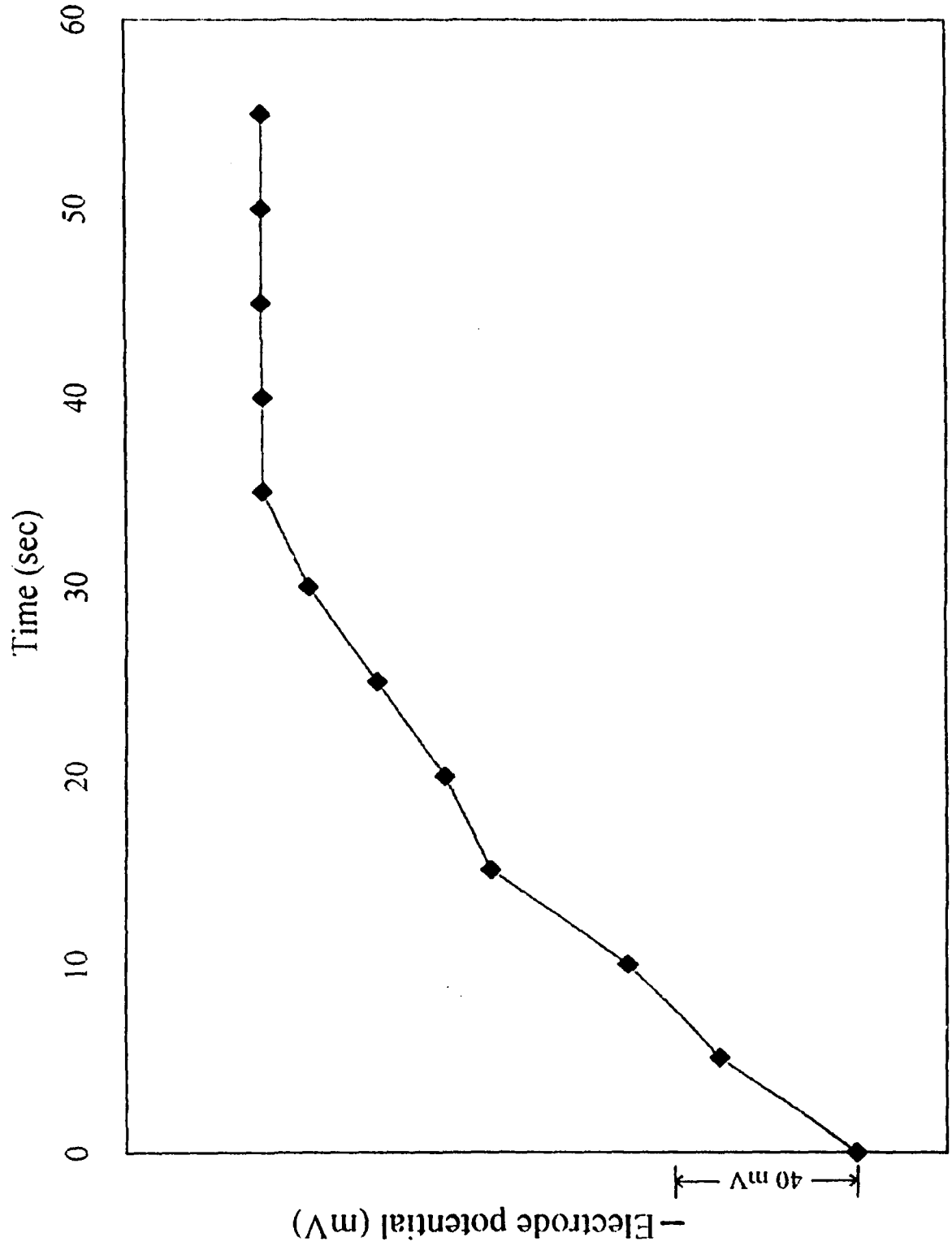

Fig. 5.2. Response of Pb^{2+} ion-selective of polypyrrole Th(IV) phosphate membrane electrode at different time interval.

It was also observed that the electrode potential remained unchanged within the pH range of 3.0-8.5 (Fig. 5.3). Hence, it is ascertained from the plot that the pH range in which the electrode potential remained constant may be taken as working pH range of the electrode. The sharp change in potentials at lower pH values (< 3) appeared to be due to interference caused by H^+ ions (co-fluxing of H^+ ions), while at higher pH values
(> 9) it may be attributed to the interference of OH^- ions (hydrolysis of Pb(II)).

The selectivity coefficients, $K_{Pb,M}^{POT}$ of various differing cation for the Pb(II) ion-selective polypyrrole Th(IV) phosphate membrane electrode were determined, by the mixed solution method [70]. The selectivity coefficient indicates the extent to which a foreign ion (M^{n+}) interferes with the response of the electrode toward its primary ions (Pb^{2+}). A scrutiny of selectivity coefficient data presented in Table 5.5, reveal that the electrode is selective for Pb(II) in presence of interfering cations. Since all the foreign metal ions interfere to a very little extent. Thus, these ions would not cause any significant interference in the determination of Pb^{2+}.

The membrane could be successfully used over a period of 3 months without any appreciable drift in potential during which the potential slope is reproducible to within ± 1 mV per concentration decade. Whenever a drift in potential was observed, the membrane was re-equilibrated with 0.1 M $Pb(NO_3)_2$ solution for 3-4 days.

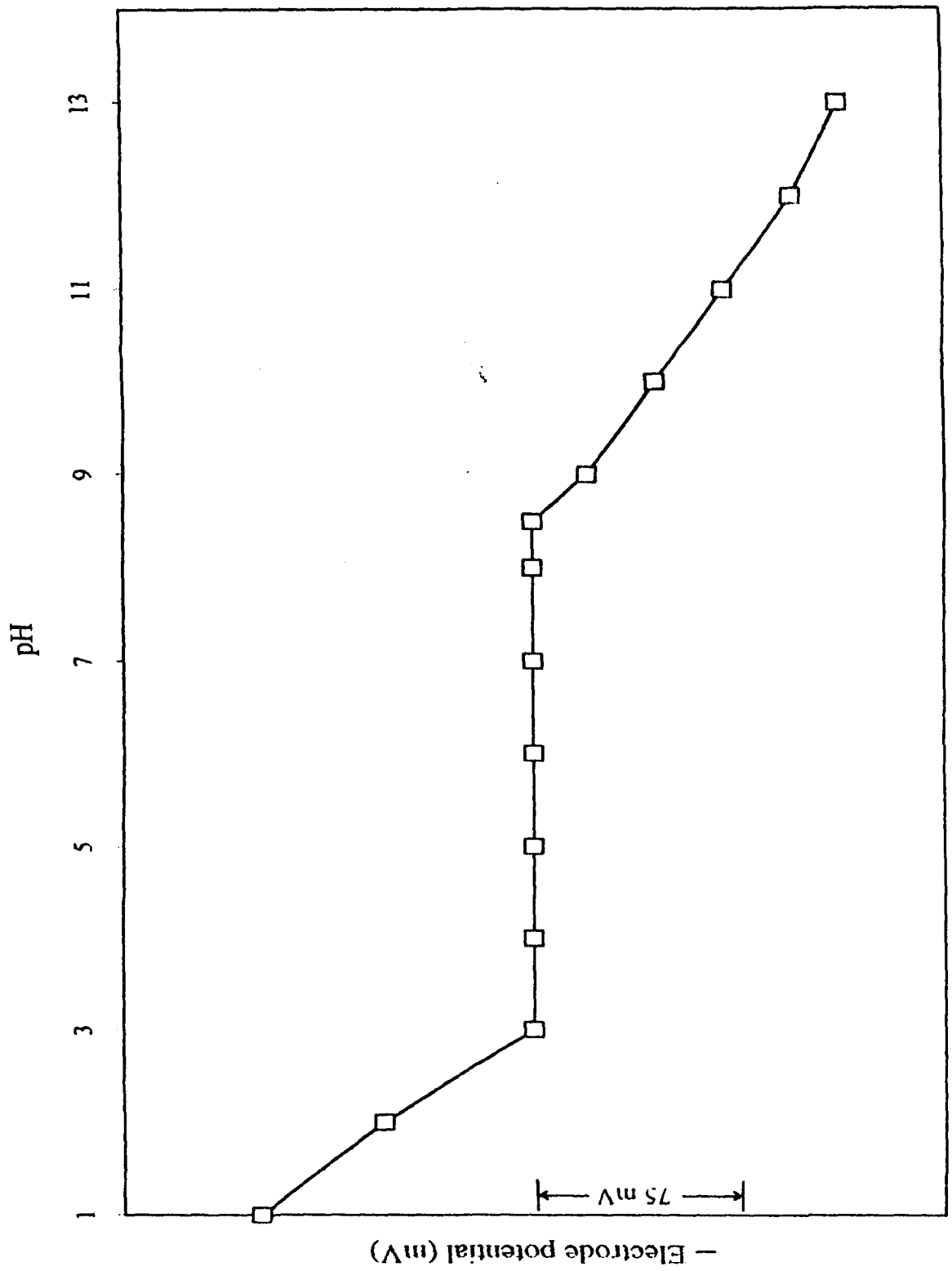

Fig. 5.3. Effect of pH on the electrode response of Pb^{2+} ion-selective the polypyrrole Th(IV) phosphate membrane electrode.

Table 5.5

Selectivity coefficient values ($K^{POT}_{Pb,M}$) for Pb^{2+} ion-selective polypyrrole Th(IV) phosphate membrane electrode for lead ions

Interfering ions (M^{n+})	Selectivity Coefficients values
Na^{+}	0.016
K^{+}	0.018
Mg^{2+}	0.024
Ca^{2+}	0.012
Sr^{2+}	0.080
Cu^{2+}	0.023
Mn^{2+}	0.011
Zn^{2+}	0.026
Hg^{2+}	0.032
Al^{3+}	0.052
Fe^{3+}	0.040

5.3.3. Potentiometric studies of heterogeneous polyaniline Sn(IV) phosphate membrane electrode

The above prepared and under investigated membrane sample S-1 of polyaniline Sn(IV) phosphate composite cation-exchanger was fabricated into ion-selective electrode and the membrane electrode was placed in 0.1 M $Hg(NO_3)_2$ solution for 5 days to get it conditioned. The choice of Hg^{2+} ions depends on its distribution behavior pattern.

After conditioning of the electrode, the potentials for a series of standard solution of the $Hg(NO_3)_2$ in the range 10^{-9} – 10^{-1} M were measured, maintaining a fixed concentration 0.1 M of Hg^{2+} ion as internal reference solution.

Potential measurement of the membrane electrode was plotted against the selected concentrations of the Hg^{2+} ions (Fig. 5.4) and showed a linear Nernstian response, as shown in Figure 5.4, for Hg(II) ions in the concentration range of 1×10^{-1}–1×10^{-6} M at a fixed ionic strength by adding a suitable excess of electrolyte with an average slope of 30 mV/decade change in concentration. Thus, the working concentration range was found to be 1×10^{-1}–1×10^{-6} M for Hg^{2+} ions. The limit of detection of this electrode for the Hg(II) ions was obtained by extrapolating the linear curve of the standard calibration to the base line at 1×10^{-6} M. This is much lower than the detection limit usually obtained in the membrane based potentiometric sensors.

The response time of stabilized electrode potential of polyaniline Sn(IV) phosphate membrane electrode (± 2 mV) for Hg^{2+} ions was determined (Table 5.2).

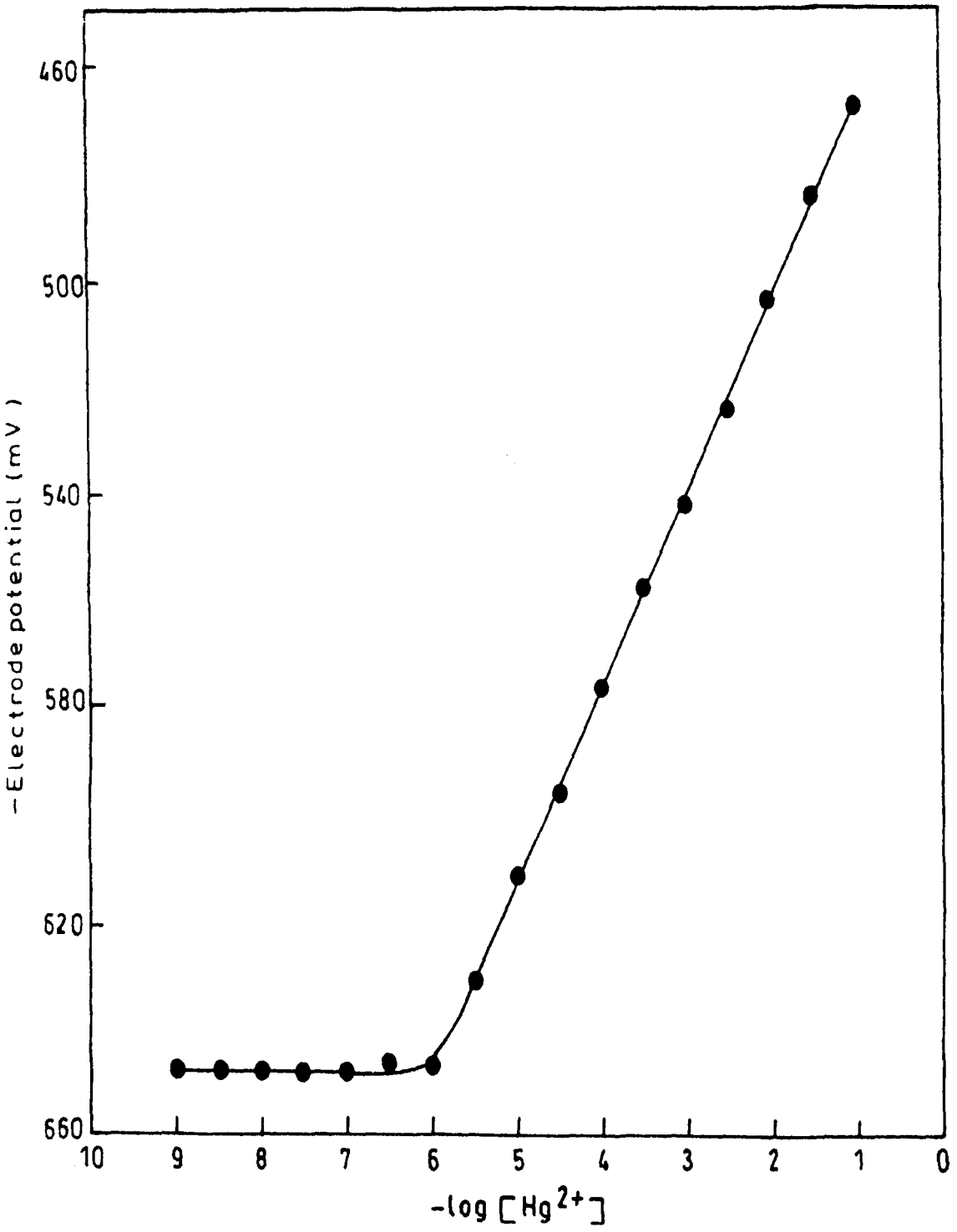

Fig. 5.4. Calibration curve for polyaniline Sn(IV) phosphate membrane electrode in aqueous solution of $Hg(NO_3)_2$.

It is observed that the static response time of the membrane sensor was found to be ~ 40 s as is evident from Fig. 5.5. Although the solid contact electrodes are often criticized for their poor response and stability, the response of this electrode is quick and the lifetime is reasonable.

The response of this membrane electrode was also significantly affected by pH (Table 5.2). As evident from Figure 5.6, electrode potential remained unchanged within the pH range of 4-9. After that pH, electrode behaved in erratic manner, which may be because mercury ions formed hydroxyl complex and precipitated. Thus, we can say that the optimum pH range of operation of this electrode was 4-9 pH.

The selectivity coefficients, $K_{Hg,M}^{POT}$ of various cations for the Hg(II) ion-selective polyaniline Sn(IV) phosphate membrane electrode at pH 4 were determined by the mixed solution method [70]. It is seen from the Figure 5.7 that alkali and alkaline earth metal ions do not interfere in the determination of mercury ions, while Cu(II), Zn(II), Pb(II), Mn(II) interfere to a very little extent and interference of Fe(III) and Al(III) was found to be negligible extent. Thus, the results revealed that the electrode is selective for Hg(II) in presence of interfering cations.

For the present polyaniline Sn(IV) phosphate membrane electrode, it was observed that measured potential of Hg^{2+} ions in the given concentration range 10^{-1}–10^{-9} was reproducible within ± 3 mV and there was no significant change in the slope of the Nernst plot during the experiment over a time period of 3 month. This suggests a longer electrode life and a stable electrode performance. However, it is very important that the performance of any ion-selective membrane electrode should be checked sooner every time before using it for any analytical purpose.

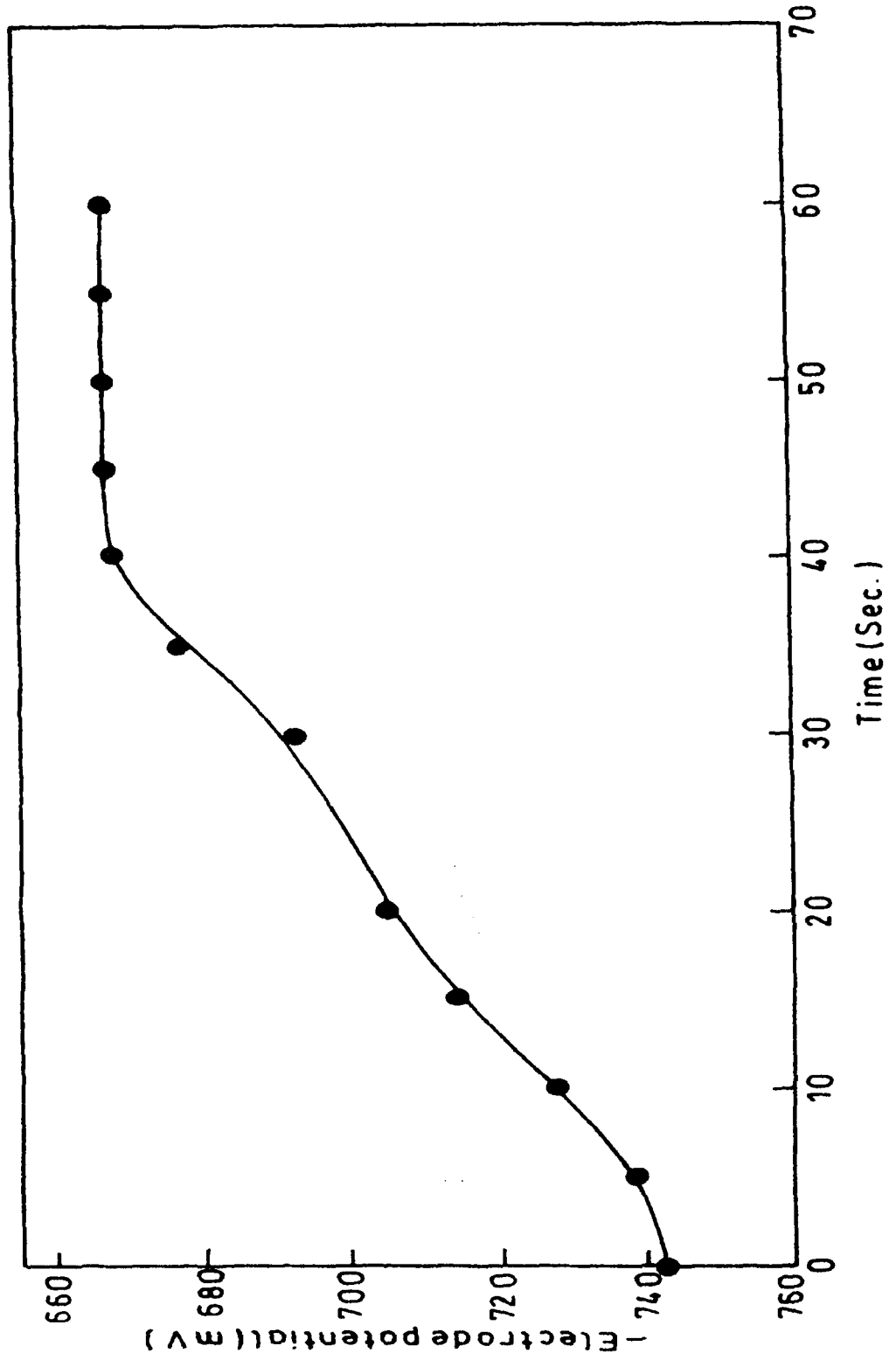

Fig. 5.5. Response of Hg^{2+} ion-selective polyaniline Sn(IV) phosphate membrane electrode at different time interval.

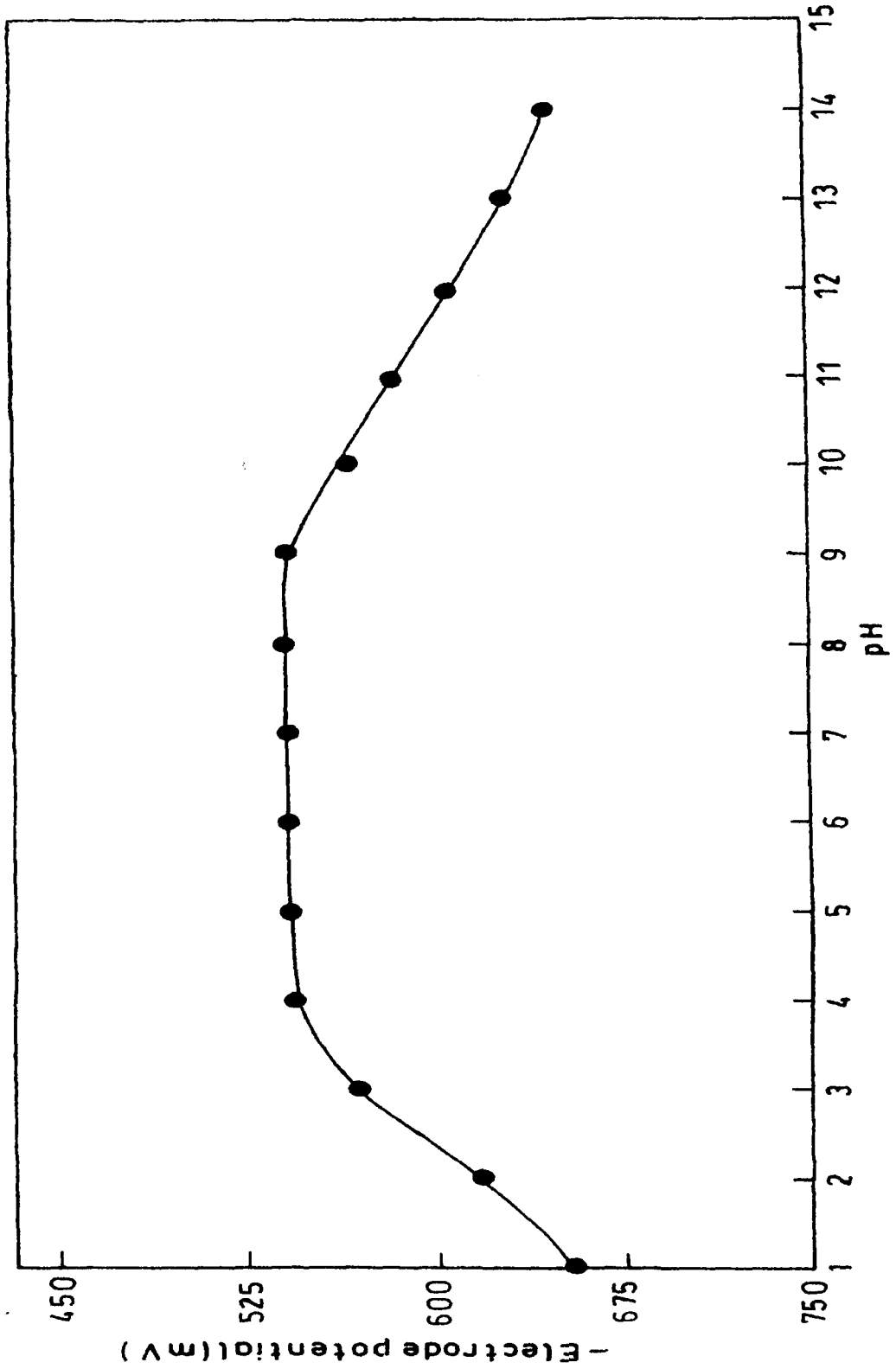

Fig. 5.6. Effect of pH on electrode response of Hg^{2+} ion-selective polyaniline Sn(IV) phosphate membrane electrode.

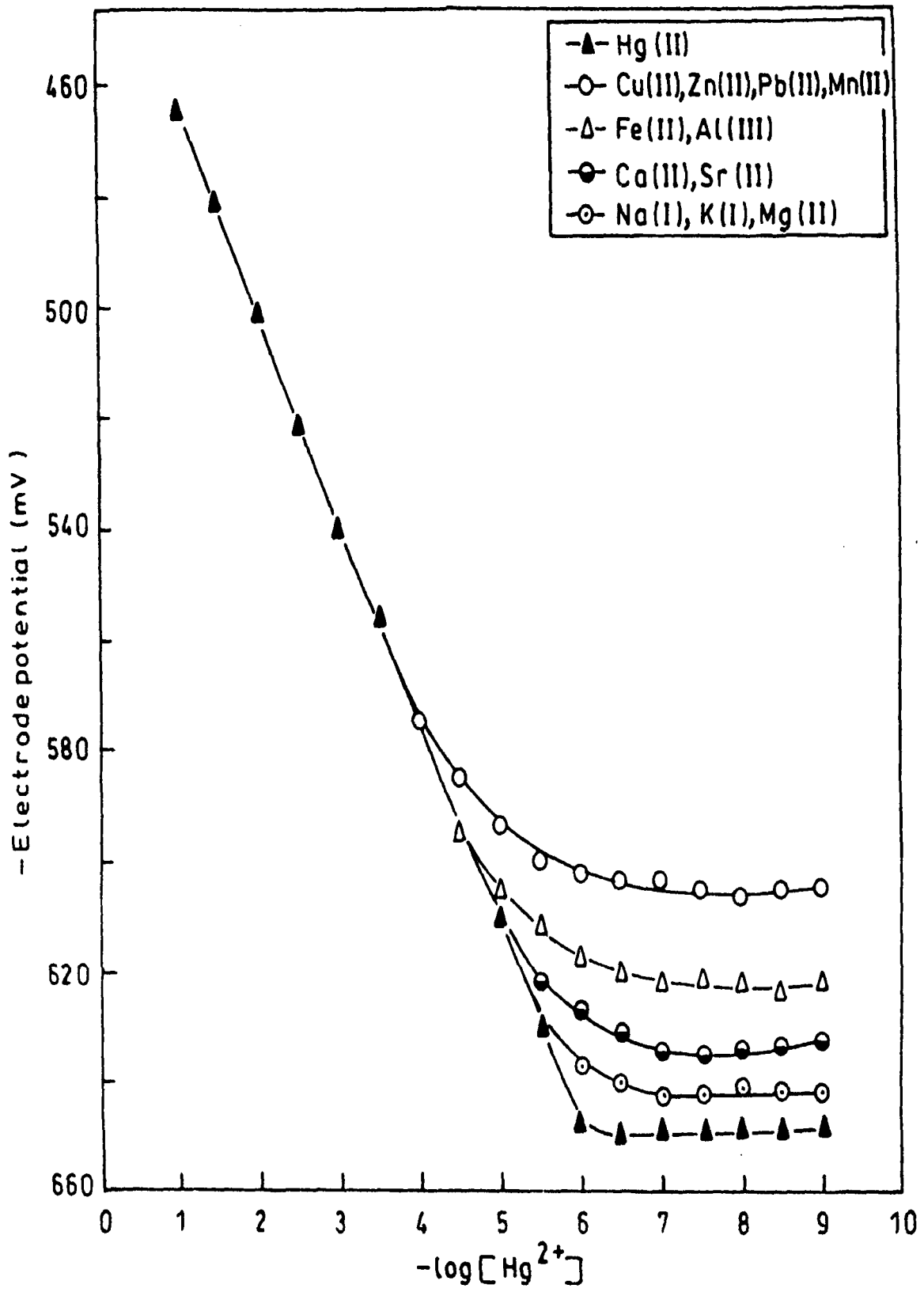

Fig. 5.7. Selectivity coefficients of various interfering ions for polyaniline Sn(IV) phosphate membrane electrode.

5.3.4. Comparison of the response characteristics of different Pb^{2+} and Hg^{2+} ion-selective membrane electrodes

A comparison of the present Pb^{2+} and Hg^{2+}-ISEs with those already reported in the literature are given in Table 5.6 and Table 5.7. From Tables, it is clear that the performance of the proposed lead and mercury(II) ion-selective membrane electrodes based on the organic-inorganic composite cation-exchangers polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate is comparable and better in many respects, such as the slope, response time, linear concentration range, life time, pH range and selectivity.

Table 5.6

Comparison of the response characteristics of different Pb^{2+} ion-selective electrodes

S. No.	Working concentration range (M)	Life time	pH range	Response time	Slope (mV)/decade	Reference
1	$1 \times 10^{-4.5}$ to $1 \times 10^{-1.7}$	2 weeks	Not mentioned	Not mentioned	25-30	77
2	1×10^{-1} to 3.2×10^{-5}	3 months	Not mentioned	10 s	29.2	78
3	1×10^{-2} to 4×10^{-6}	3 months	2.0-7.0	70 s	29.0	79
4	1×10^{-2} to 3×10^{-6}	Not mentioned	Not mentioned	Not mentioned	30.1	80
5	8×10^{-3} to 1×10^{-6}	2 months	3.0-6.0	40 s	29	81
6	1×10^{-1} to 1×10^{-6}	2 months	3.0-6.0	14 s	28.7	82
7	1×10^{-2} to 1×10^{-5}	3 months	4.5-7.0	15 s	29.0	83
8	1×10^{-1} to 5×10^{-6}	3 months	3.0-8.0	35 s	29.17	Proposed assembly

Table 5.7

Comparison of the response characteristics of different Hg^{2+} ion-selective electrodes

S. No.	Working concentration range (M)	Life time	pH range	Response time	Slope (mV)/decade	Reference
1	1×10^{-1} to 1×10^{-5}	Not mentioned	Not mentioned	Not mentioned	58.0	84
2	1×10^{-1} to 1×10^{-4}	NM	2.0-12.8	Not mentioned	27.0	85
3	1×10^{-1} to 1×10^{-5}	5 weeks	1.0	4 min.	Not mentioned	86
4	1×10^{-1} to 1×10^{-5}	5 weeks	0-2.0	Less than 3 min.	28.5	87
5	1×10^{-1} to 1×10^{-5}	3 months	2.8-3.9	30-40 s	29.0	88
6	1×10^{-1} to 1×10^{-4}	4 months	2.8-4.2	30-40 s	28.5	89
7	1×10^{-1} to 1×10^{-5}	2 months	0.5-3.5	20-100 s	28.5	90
8	1×10^{-1} to 1×10^{-5}	2 months	0.5-2.5	20-100 s	29.6	90
9	1×10^{-1} to 5×10^{-5}	3 months	1.3-4.0	20 s	27.3	91
10	1×10^{-1} to 1×10^{-6}	3 months	4.0-9.0	40 s	30	Proposed assembly

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Chapter 6

Analytical Applications of Polypyrrole Th(IV) phosphate and Polyaniline Sn(IV) phosphate Composite Cation-Exchangers

- *Separation of metal ions*
- *Determination of Pb(II) & Hg(II) from samples of waste water using ion-selective electrodes*
- *Adsorption of pesticides*

Chapter 6

6.1. Introduction

Environmental problem is the most important and burning problem of today. Water pollution due to the release of industrial and domestic wastewater has already become a serious matter. The common practice adopted so far includes the discharge of the untreated or partially treated industrial effluent into public sewers, rivers, sea and on land. Heavy metals when present in water in concentrations exceeding the permitted limits are injurious to the health. Hence, it is very important to treat such waters to remove the metal ions present before it is supplied for any useful purpose. When we need to remove a particular ion in presence of other, we need a material specific for that particular metal ion and a devise to determine the concentration level. Thus by synthesizing new 'organic-inorganic' composite ion exchangers having selectivity for particular metal ion, we can separate the undesired metal from the effluents such as Cd, Pb, Hg, Cr, Ni, Sn, Cu, Co, As, and Zn. A large number of such composite materials possessing the selectivity for heavy toxic metal ions have been prepared in our laboratory and are being utilized in environmental water pollution analysis [1-9]. Secondly 'organic-inorganic' electrically conducting composite ion exchangers can be used in the preparation of sensitive and selective ion-sensors, potentiometer sensor, chemical sensors, or more commonly ion-selective electrodes (ISEs) for the determination of heavy toxic metal ions in the waste water samples. Therefore, these composite ion-exchangers have well established their

position in separation science and technology, and have been employed in the selective separation and preconcentration of metal ions as well as recovery of heavy toxic metals from various waste effluents to decrease the pollution load in the environment [10-18].

Lead is used in alloys, lead-acid batteries and solder amongst other applications. Organic forms, tetramethyl- and tetraethyl-lead were used extensively as anti-knock and lubricating components of petrol, but this is being phased out due to the toxicity of this metal. Subsequently, intake is predominantly from ingesting foods and drinking water, due to dissolution from domestic tap water pipes and connections, and not from atmospheric emissions that are in decline.

On the other hand, mercury usage is also in decline due to the acute toxicity of the inorganic and organic forms of this metal. Its applications include as a cathode in chloroalkali cells, as a fungicide, as a catalyst for polymer production and in the cosmetics and pharmaceutical industry. The inorganic form is readily converted via biotic and abiotic processes in aquatic habitats to form alkylated lipophilic neurotoxic species which bioaccumulate in freshwater and marine organisms. Inorganic mercury is typically found at concentrations < 0.5 $\mu g\ L^{-1}$ in ground and surface waters. The predominant organic forms are methyl-, ethyl- and phenylmercury, which can biomagnify up through the food chain far more readily than inorganic forms and result in chronic human exposure. The ingestion of fish and related products is a primary source of exposure, and there has been alarming evidence of the presence of methyl-mercury in fish-based foods in both the UK (Food Standards Agency, May 2002) and worldwide (Food and Agriculture Organization of the United

Nations/WHO, June 2003, JECFA/61/SC). The WHO guidelines for drinking water quality stipulate allowable concentrations of 0.01 and 0.001 mg L^{-1} for Pb(II) and Hg(II).

Since these composite materials i.e. polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate were found highly selective for lead and mercury respectively, as shown from the selectivity studies performed in Chapter-3 (Section 3.2.4.6.); the utility of these cation-exchangers has been explored for the quantitative separations of Pb^{2+} and Hg^{2+} from some binary mixtures as well as removal of these toxic metals from some synthetic samples. Therefore, in this chapter, we have studied some analytical and environmental applications of these composite materials used in separation of metal ions, as adsorbent and ion-selective membrane electrode.

Pesticides have a judicious use in agriculture; therefore their adsorption behavior is an important aspect of study. One of the important environmental applications of these ion-exchangers is to adsorb pesticides on their surfaces. Thermodynamics (equilibrium studies) is a fundamental approach for describing equilibria and helps in evaluating the adsorption/exchange process occurring on the surface of the ion-exchangers.

The presence of an ion-exchange material possessing a good ion-exchange capacity may enhance the adsorption characteristics of the soil. The adsorption of pesticides on soils has been a significant feature [19-22]. It is affected by the presence of metal ions, which play an important role in modifying the nutritional status of the soils. Inorganic ion-exchangers are known to be selective for metal ions and hence their presence in soil may have some far reaching consequences [23,24].

They could effect a greater retention of metal ions in soil owing to their ion-exchange behavior, thus preventing them from entering into crops and ultimately to the food chain. These materials have been found to absorb pesticides to a much greater extent than the ordinary soils, for example antimony(V) silicate [25] prepared in these laboratories has shown about a ten-fold enhanced adsorption potential for the pesticide carbofuran as compared to soils. In order to extend such a study, polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers having better ion-exchange capacity, *i.e.* 1.56 meq dry g^{-1} as compared to inorganic cation-exchanger Th(IV) phosphate 0.72 meq dry g^{-1} [5] and 1.96 meq dry g^{-1} as compared to Sn(IV) phosphate 1.12 meq dry g^{-1} [26], respectively were selected. The adsorption properties on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate were observed for the adsorption of trichloroacetic acid (Cl_3CCOOH) and mancozeb, respectively. Trichloroacetic acid (TCA) is considered a ubiquitous, toxic and phytotoxic compound, with herbicidal properties. While Mancozeb is one member of ethylenebisdithiocarbamate (EBDC) fungicides. Mancozeb is used to protect many fruit, vegetable, nut and field crops against a wide spectrum of fungal diseases, including potato blight, leaf spot, scab (on apples and pears), and rust (on roses). It is also used for seed treatment of cotton, potatoes, corn, sunflower, sorghum, peanuts, tomatoes, flax and cereal grains. Mancozeb is available as dusts, liquids, water dispersible granules, as wettable powders and as ready-to-use formulations. It may be commonly found in combination with zineb and maneb. This is an organophosphate compound used commonly as an insecticide in agricultural, household and public health uses to control different types of insects.

6.2. Experimental

6.2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-merck, Ciba-Geigy and Qualigens (India Ltd.). All other reagents and chemicals were of analytical reagent grade. A digital pH-meter (Elico LI-10, India), a temperature controlled shaker and a digital potentiometer (Equiptronics EQ 609, India) with saturated calomel electrodes as reference electrodes were used.

6.2.2. Preparation of polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers and ion-selective electrodes

Various samples of 'organic-inorganic' composite cation-exchange materials 'polypyrrole Th(IV) phosphate' and 'polyaniline Sn(IV) phosphate' were prepared as described in Chapter – 2 (Section 2.2.3.). But the sample S-5 (Table 2.1) and sample T-7 (Table 2.2) were selected for the studies of their analytical applications, as an adsorbent for pesticides and potentiometric sensor. The preparation of ion-exchange membrane and fabrication of ion-selective electrode was done as described in Chapter – 5 (Section 5.2.3. and 5.2.5.).

6.2.3. Analytical applications of the composites

6.2.3.1. Quantitative separations of metal ions using composite cation-exchangers

On the basis of K_d values (distribution studies) of sample S-5 and sample T-7,

as described in Chapter 3 (Section 3.2.4.6), these samples were selected to achieve quantitative binary separations of some important metal ions of analytical utility on polypyrrole Th(IV) phosphate and polyanilne Sn(IV) phosphate columns. 1 g of both of the materials, S-5 and T-7 (~ 125 μm particle size) in H^+-form were used for column separations in two different glass tubes having an internal diameter of ~ 0.6 cm and a height of 35 cm. The columns were washed thoroughly with DMW. The mixture of two metal ions having initial concentrations of 0.01 M each was loaded on the both columns and allowed for one hour to absorb the metal ions on the exchangers. The mixture was then passed on to the columns gently (maintaining a flow rate of 2-3 drops per minute) till the level was above the surface of the materials. After recycling two or three times to ensure complete adsorption of the mixture on column beads, the separations were achieved by passing a suitable solvent at a flow rate of 1 ml min^{-1} through both the columns as eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration [27].

6.2.3.2. Removal of Pb^{2+} and Hg^{2+} from water samples using composite cation-exchangers

Since polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers, sample S-5 and T-7 (Table 2.1 and Table 2.2 in Chapter - 2) showed the highest selectivity for Pb^{2+} and Hg^{2+} (Table 3.9 and Table 3.10 in Chapter - 3) respectively, in comparison to other metal ions. Removal of Pb^{2+} and Hg^{2+}, i.e., preconcentration of Pb^{2+} and Hg^{2+} from water samples were examined by passing various volumes of aqueous solutions (containing Pb^{2+} and Hg^{2+}) at a pH

4.5 through the two different columns (30 cm × 0.4 cm^2) packed with 1 g composite cation-exchanger each, respectively. Pb^{2+} and Hg^{2+} retained on the columns could be eluted quantitatively by passing the suitable eluent through the columns at a flow rate of 1 ml min^{-1}.

6.2.3.3. Determination of metal ions in real waste water samples using the ion-selective membrane electrodes

6.2.3.3.1. Analysis of wastewater samples containing Pb^{2+} and Hg^{2+} using the polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate membrane electrodes

Polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate based Pb^{2+} and Hg^{2+} ion-selective membrane electrodes were applied to the direct measurement of Pb^{2+} and Hg^{2+} in the drain waters collected from Department of Chemistry and Department of Applied Chemistry, Aligarh Muslim University, Aligarh, (India) respectively. The samples were collected by a routine technique from five different locations of drains and preserved with HNO_3, stored in glass bottles and analyzed within 12 h after collection. Since the samples contain particulate matters, they were centrifuged and the potentials were measured after adjusting the pH ≈ 4 with HNO_3 or NH_3. Three replicate measurements were done to obtain the lead contents in five samples with this electrode using the membrane sensor's calibration graph.

6.2.3.3.2. Determination of Pb^{2+} and Hg^{2+} by potentiometric titrations using the polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate membrane electrodes

The lead and mercury selective membrane electrodes were employed as indicator electrodes in the titration of 1.0×10^{-2} M $Pb(NO_3)_2$ and 1.0×10^{-2} M $Hg(NO_3)_2$ solutions, respectively against 1.0×10^{-2} M EDTA solution as a titrant. For this, 5 ml of $Pb(NO_3)_2$ and $Hg(NO_3)_2$ solutions were pippeted out in two different beakers. The volume of each beaker was raised upto 20 ml by DMW. These solutions were titrated with EDTA solution and electrode potential were measured after each addition of 0.5 ml of $Pb(NO_3)_2$ and $Hg(NO_3)_2$ solutions, respectively. The necessary adjustment of pH ($\approx$ 4) was made before adding the titrant. Potential values were plotted against the volume of EDTA used.

6.2.3.4. Adsorption of pesticide (trichloroacetic acid) on polypyrrole Th(IV) phosphate composite cation-exchanger

6.2.3.4.1. Preparation of reagents

Trichloroacetic acid solutions of different molarities ranging from 0.1-0.6 M and 0.1 M NaOH solution were prepared in demineralized water (DMW).

6.2.3.4.2. Adsorption Thermodynamics

A total of 0.5 g portions of the polypyrrole Th(IV) phosphate composite cation-exchanger were placed in various stoppered conical flasks containing 2 ml trichloroacetic acid of different concentrations varying from 0.01-0.06 M followed by

the addition of 30 ml DMW to dilute the solutions, at the desired temperatures (30, 45 and 60 °C). The mixtures were shaken for 70 min, each to attain equilibrium. The concentrations of trichloroacetic acid before and after adsorption were analyzed by titrating against a standard solution of 0.1 M NaOH.

6.2.3.5. Adsorption of pesticide (mancozeb) on polyaniline Sn(IV) phosphate composite cation-exchanger

6.2.3.5.1. Preparation of reagents

Mancozeb suspensions of different molarities ranging from 0.01-0.06 M were prepared in demineralized water (DMW). 0.1 N Iodine solution was prepared in potassium iodide followed by DMW. 10% lead acetate solution was prepared in DMW, while 2 N potassium hydroxide in methanol.

6.2.3.5.2. Adsorption Thermodynamics

A total of 0.5 g portions of the polyaniline Sn(IV) phosphate composite cation-exchanger were placed in various stoppered conical flasks at the desired temperatures (25, 35 and 45 °C) followed by the addition of 10 ml mancozeb suspensions of different concentrations varying from 0.01-0.06 M and the mixtures were shaken for 70 min, each to attain equilibrium. The concentrations of mancozeb before and after adsorption were analyzed by iodometrically as given below.

6.2.3.5.3. Traditional CS_2 reaction system

The system proposed by Cullen [28] consists of a two-necked round bottom flask connected to a condenser, which is connected to two traps in series. CS_2 formed

after hydrolysis of mancozeb taken in round bottom flask carrying into the first trap containing lead acetate [$Pb(CH_3COO)_2$] solution to aid in the removal of interferences. After that CS_2 is reacted with methanolic KOH present in the second trap and the xanthate formed is titrated with I_2 solution.

6.3. Results and Discussions

6.3.1. Quantitative separation of metal ions using composite cation-exchangers

On the basis of distribution studies, the most promising property of these materials was found to be the high selectivity towards Pb(II) and Hg(II), (major polluting elements in the environment), indicating importance in environmental studies. The separation capability of the material polypyrrole Th(IV) phosphate has been demonstrated by achieving some important binary separations of different synthetic metal mixtures involving Pb(II), for example: Pb^{2+}-Zn^{2+}, Pb^{2+}-Mg^{2+}, Pb^{2+}-Al^{3+}, Zn^{2+}-Hg^{2+}, $Fe3^{+}$-Hg^{2+}, Pb^{2+}-Cd^{2+}, Pb^{2+}-Cu^{2+} and Pb^{2+}-Ni^{2+}. Table 6.1 summarizes the salient features of these separations. The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). It was observed that Pb(II) retained strongly on the cation-exchanger column. The weakly retained metal ions appear out of the column faster than Pb(II) and Pb(II) was eluted after by $HClO_4$ solution. The order of elution and eluents used for some representative binary separations are also illustrated in Fig. 6.1. The separations are quite sharp and recovery is quantitative and reproducible. It was also observed from the distribution studies that the cation-exchanger was also found to be selective for Hg(II). Some binary separations Hg^{2+}-Zn^{2+}, Fe^{3+}-Hg^{2+}, were also carried out on the proposed composite cation-exchanger column (Table 6.1).

On the basis of distribution studies, the most promising property of the composite cation-exchanger polyaniline Sn(IV) phosphate was found to be the high

Table 6.1

Some binary separation of metal ions achieved on polypyrrole Th(IV) phosphate

Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluent used	Volume of eluent (ml)
Zn(II)	1307.4	1294.3	- 1.00	0.01 M HNO_3	50
Pb(II)	4144.0	4144.0	0.00	0.1 M $HClO_4$	60
Mg(II)	729.2	731.6	+ 0.33	DMW	60
Pb(II)	3108.0	3087.3	- 0.67	0.1 M $HClO_4$	50
Al(III)	809.4	808.1	- 0.16	0.01 M $HClO_4$	60
Pb(II)	3108.4	3159.8	+ 1.65	0.1 M $HClO_4$	50
Zn(II)	1307.4	1307.4	0.00	0.01 M HNO_3	50
Hg(II)	3510.3	3560.5	+ 1.43	0.1 M HCl	60
Fe(III)	1117.0	1111.5	- 0.49	0.01 M $HClO_4$	50
Hg(II)	3008.9	3028.9	+ 0.66	0.1 M HCl	50
Cd (II)	2248.0	2231.14	-0.75	0.01 M HNO_3	50
Pb (II)	4144.0	4092.2	-1.25	0.1 M $HClO_4$	60
Cu (II)	1271.0	1267.82	-2.5	0.01 M HNO_3	50
Pb (II)	4144.0	4216.52	+1.75	0.1 M $HClO_4$	60
Ni (II)	1174.2	1168.33	-0.5	0.01 M HNO_3	60
Pb (II)	4144.0	4175.08	+0.75	0.1 M $HClO_4$	60

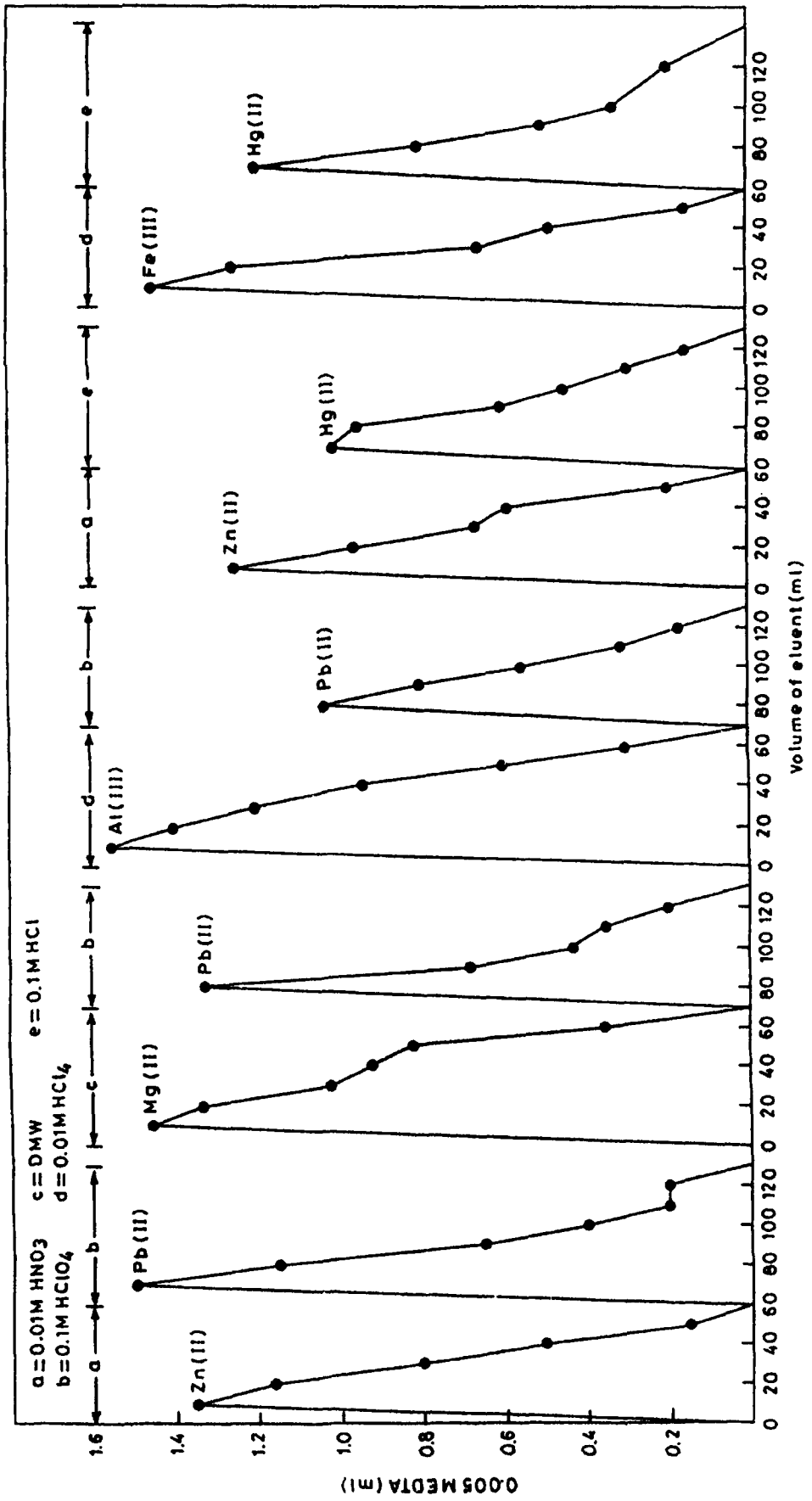

Fig. 6.1. Some binary separation of metal ions achieved on polypyrrole Th(IV) phosphate columns.

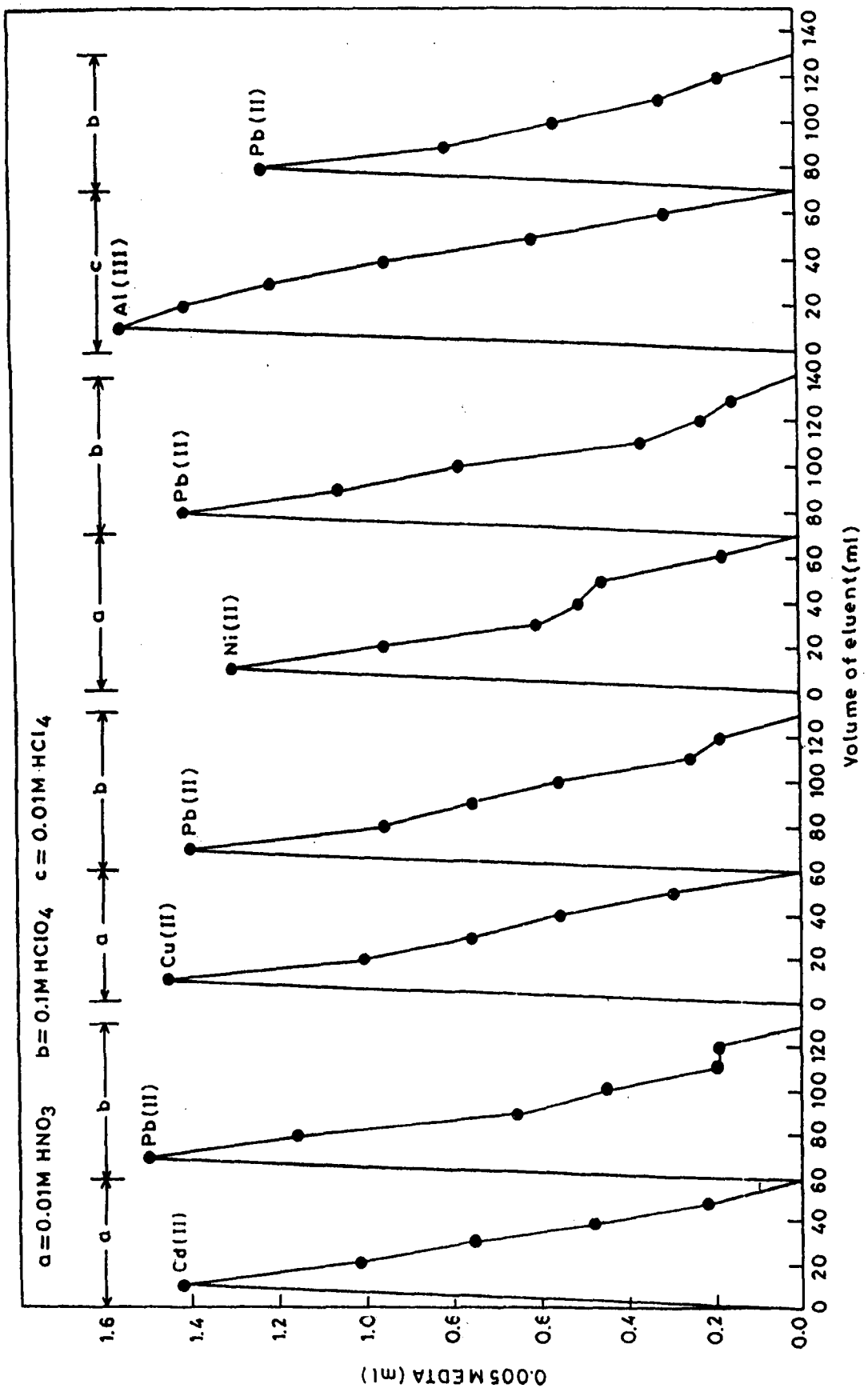

Fig. 6.1. Continued.

selectivity towards Hg(II). The separation capability of the material has been demonstrated by achieving some important binary separations of different synthetic metal mixtures involving Hg(II), for example: Hg^{2+}-Cu^{2+}, Hg^{2+}-Ni^{2+}, Hg^{2+}-Cd^{2+}, Hg^{2+}-Co^{2+} and Hg^{2+}-Al^{3+}. Table 6.2 summarizes the salient features of these separations. The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). The order of elution and eluents used for these separations are also illustrated in Fig. 6.2. The separations are quite sharp and recovery is quantitative and reproducible. It may also be observed from the distribution studies that the cation-exchanger was also found to be selective for Pb(II). Some binary separations Pb(II)-Mg(II), Pb(II)-Zn(II), Pb(II)-Ba(II), Pb(II)-Sr(II), Pb(II)-Bi(III), Pb(II)-Fe(III) were also carried out on the proposed composite cation-exchanger column (Table 6.2). The order of elution and eluents used for these separations are also illustrated in Fig. 6.2.

6.3.2. Removal of Pb^{2+} and Hg^{2+} from water samples using composite cation-exchangers

Since polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate composite cation-exchangers were found highly selective for Pb^{2+} and Hg^{2+} ions, respectively, an attempt has been made for the selective removal of Pb^{2+} and Hg^{2+} from water. The results of removal studies of Pb^{2+} and Hg^{2+} from aqueous samples are presented in Table 6.3 and Table 6.4. It was observed from the data that the recovery is quantitative and reproducible.

Table 6.2

Some binary separation of metal ions achieved on polyaniline Sn(IV) phosphate composite cation-exchanger

Separation achieved	Amount loaded (μg)	Amount found (μg)	% difference	Eluent used	Volume of eluent (ml)
Cu(II)	953.10	949.92	- 0.33	0.01 M HCl	50
Hg(II)	2005.90	1995.87	- 0.50	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Ni(II)	1467.75	1467.75	0.00	0.01 M HCl	60
Hg(II)	3008.85	2998.82	- 0.33	0.1M HNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Cd(II)	2248.00	2242.38	- 0.25	0.1 M HCl	50
Hg(II)	3510.33	3490.27	- 0.57	0.1 MHNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Co(II)	883.95	875.11	- 1.00	0.01 M HCl	50
Hg(II)	3008.85	3008.85	0.00	0.1 MHNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Mg(II)	850.66	849.45	- 0.14	0.1 M HNO_3	60
Pb(II)	4144.00	4144.00	0.00	0.1 M HCl	50
Zn(II)	1307.40	1310.67	+ 0.25	0.1 M HCl	60
Pb(II)	3108.00	3097.64	- 0.33	0.1 M HNO_3 + 0.1 M NH_4NO_3	50
Ba(II)	2059.5	20458.7	- 0.67	0.1 M HNO_3	50
Pb(II)	4144.0	7 4133.64	- 0.25	0.1M HNO_3 + 0.1 M NH_4NO_3	50
Sr(II)	876.2	884.96	+ 0.99	0.1 M HCl	50
Pb(II)	3108.0	3108.00	0.00	0.1 M HNO_3 + 0.1 M NH_4NO_3	50
Bi(III)	2089.8	2110.70	+ 1.00	0.1MCH_3COOH+0.1MCH_3COONa	50
Pb(II)	3626.00	3615.64	- 0.27	0.1 MHNO_3 + 0.1 M NH_4NO_3	50
Fe(III)	1116.80	1111.23	- 0.50	0.1 M HCl	50
Pb(II)	2590.00	2610.00	+ 0.77	0.1 MHNO_3 + 0.1 M NH_4NO_3	50

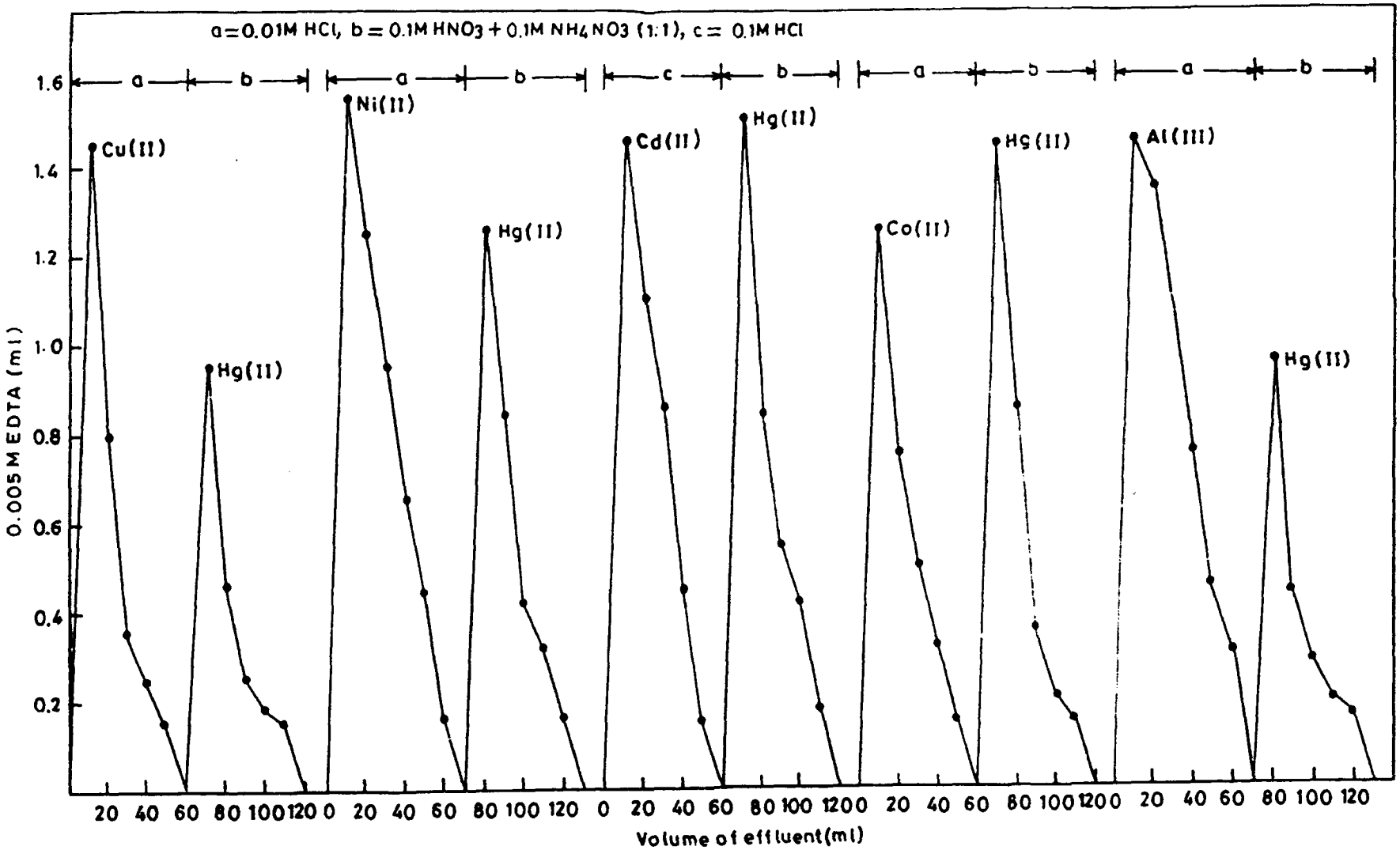

Fig. 6.2. Some binary separation of metal ions achieved on polyaniline Sn(IV) phosphate columns.

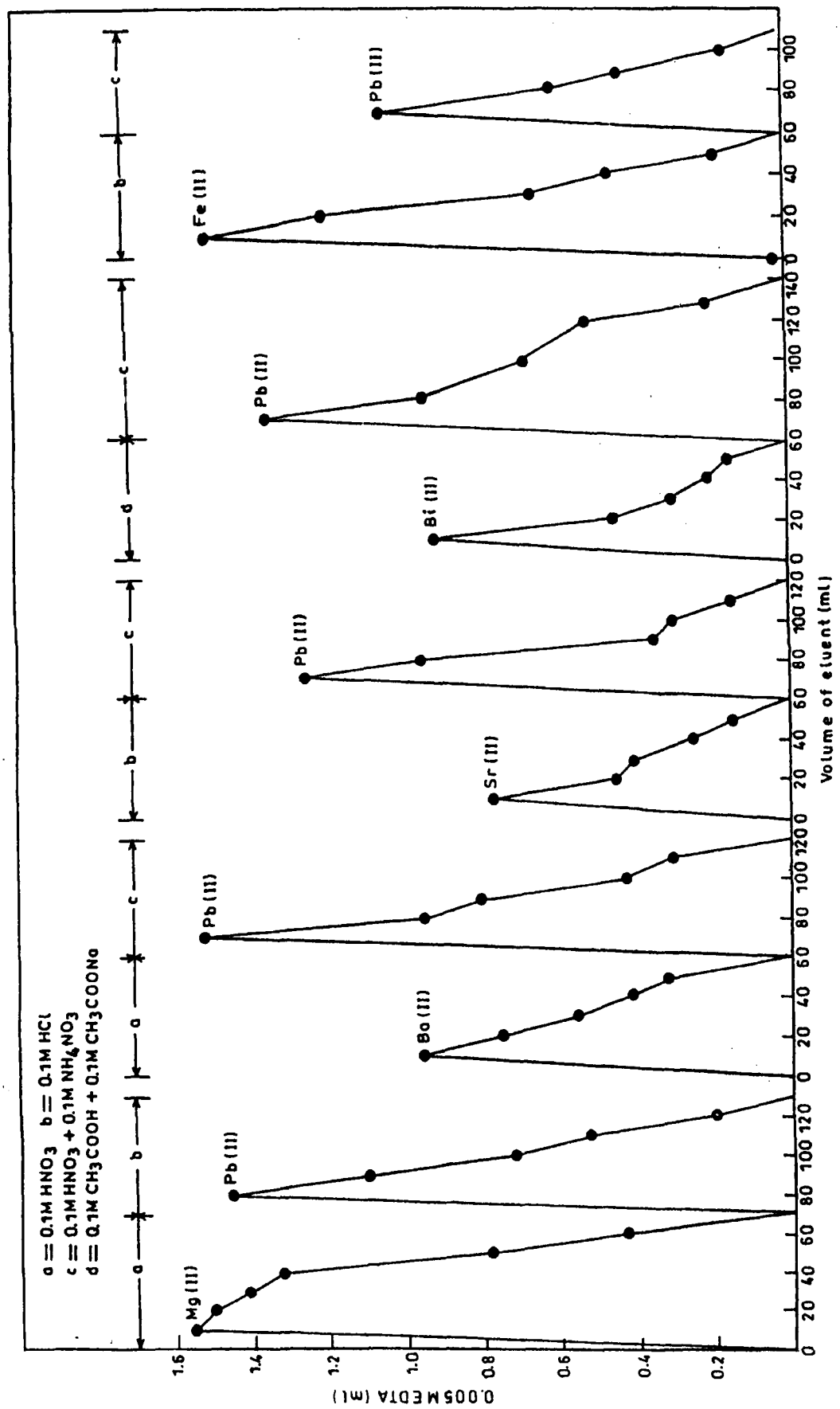

Fig. 6.2. Continued

Table 6.3

Removal of Pb^{2+} from water samples using polypyrrole Th(IV) phosphate column

Total volume of test solution (ml)	Amount of Pb^{2+} taken (mg)	pH of the solution	Flow rate (ml min^{-1})	Pb^{2+} removal (%)
250	10	4.5	4	100 ± 0.2
250	20	4.5	4	100 ± 0.2
250	30	4.5	3	100 ± 0.4
400	50	4.5	2	100± 0.1
500	75	4.5	2	99 ± 0.9
500	100	4.5	4	95 ± 0.6
500	150	4.5	4	96 ± 0.5
700	200	4.5	2	96 ± 0.5
800	300	4.5	2	97± 0.5
850	500	4.5	2	96 ± 0.8
1000	600	4.5	2	98± 0.8

Table 6.4

Removal of Hg^{2+} from water samples using polyaniline Sn(IV) phosphate column

Total volume of test solution (ml)	Amount of Hg^{2+} taken (mg)	pH of the solution	Flow rate (ml min^{-1})	Hg^{2+} removal (%)
250	10	4.5	4	100 ± 0.2
250	20	4.5	4	100 ± 0.2
250	30	4.5	3	100 ± 0.4
400	50	4.5	2	100± 0.1
500	75	4.5	2	100± 0.8
500	100	4.5	4	97 ± 0.9
500	150	4.5	4	94 ± 0.7
700	200	4.5	2	94 ± 0.6
800	300	4.5	2	94± 0.6
850	500	4.5	2	94 ± 0.7
1000	600	4.5	2	93± 0.2

6.3.3. Analysis of wastewater samples containing Pb^{2+} and Hg^{2+} using the polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate membrane electrodes

The direct potentiometeric measurement of concentration of Pb^{2+} and Hg^{2+} in the drain waters samples collected from Department of Chemistry and Department of Applied Chemistry, Aligarh Muslim University, Aligarh, (India) respectively, showed that the concentration of Pb(II) in the drain water of Department of Chemistry, A.M.U., Aligarh, was found to be 1 M, while the concentration of Hg(II) in the drain water samples of Department of Applied Chemistry, A.M.U., Aligarh, was found to be 10^{-3} M.

6.3.4. Determination of Pb^{2+} and Hg^{2+} by potentiometric titrations using the polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate membrane electrodes

The practical utility of the proposed membrane sensors assembly was tested by using as indicator electrodes in the potentiometric titration of Pb(II) and Hg(II) with EDTA. The addition of EDTA causes a decrease in potential as a result of the decrease in free Pb(II) and Hg(II), respectively, ion concentration due to the complexation with EDTA as shown in Fig. 6.3 and Fig. 6.4. The amount of Pb(II) and Hg(II) ions in solution can be accurately determined from the resulting neat titration curves providing a sharp rise in the titration curve at the equivalence point.

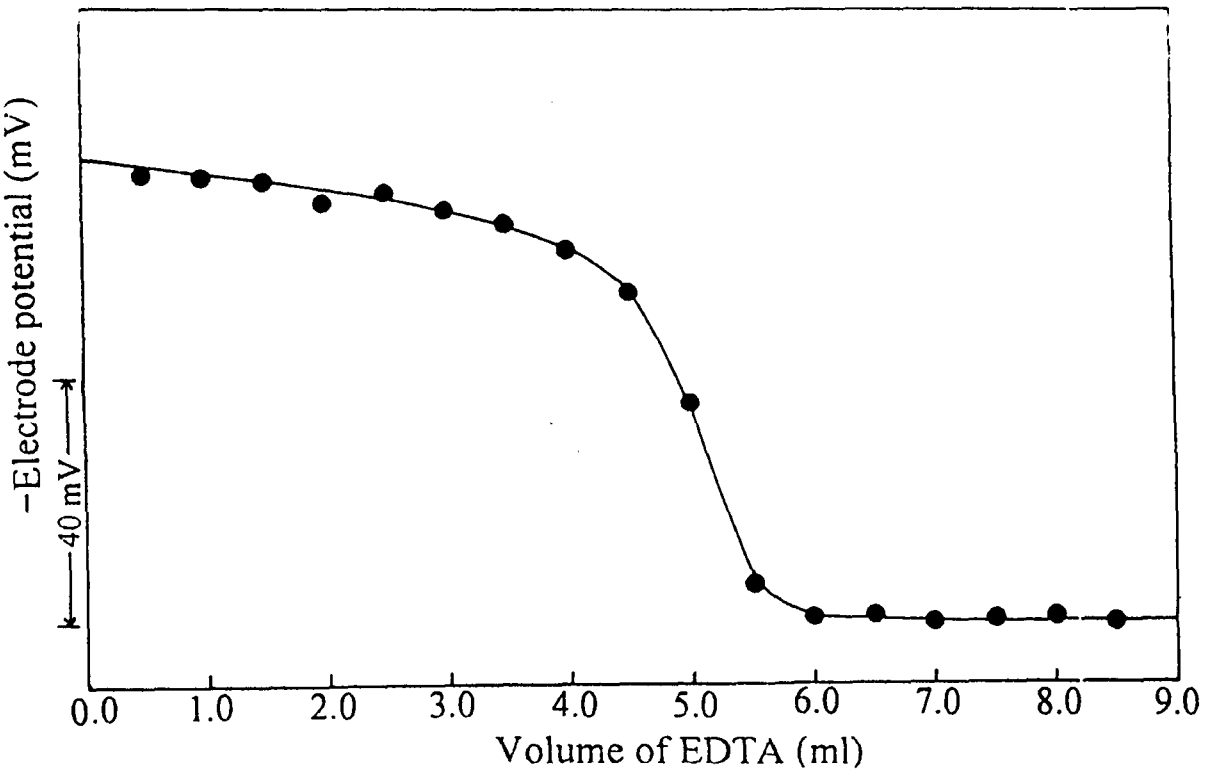

Fig. 6.3. Precipitation titration of Pb(II) against EDTA solution.

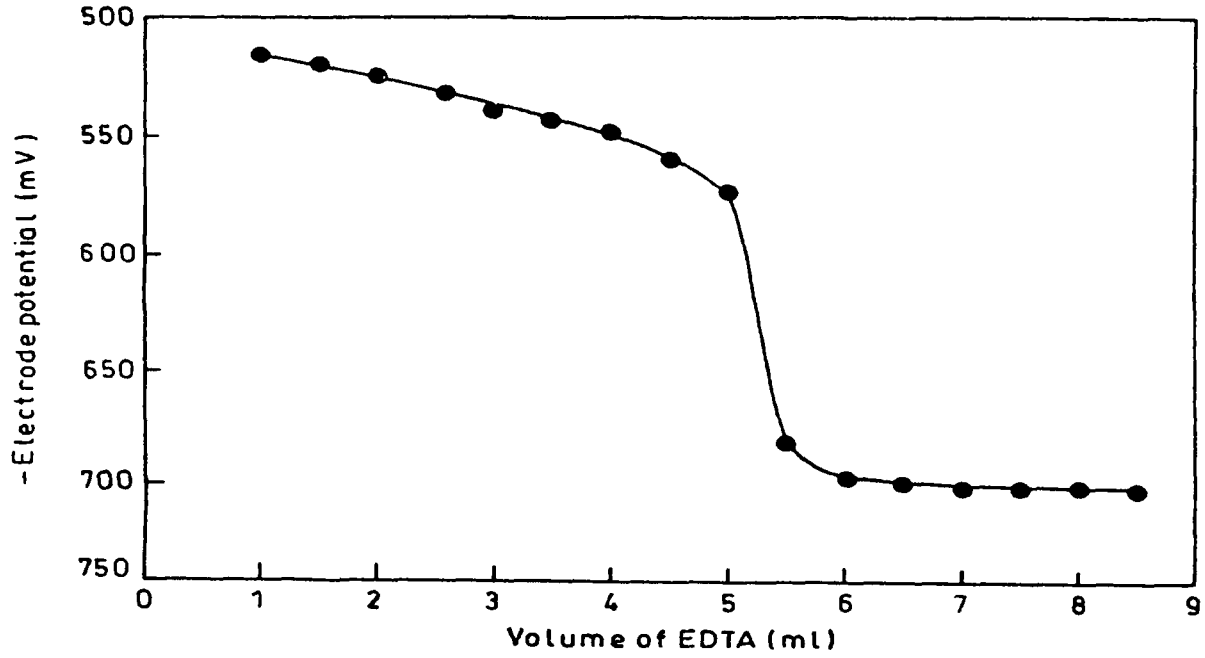

Fig. 6.4. Precipitation titration of Hg(II) against EDTA solution.

6.3.5. Adsorption of pesticides trichloroacetic acid & mancozeb on polypyrrole Th(IV) phosphate & polyaniline Sn(IV) phosphate composite cation-exchangers

The adsorption isotherms of polypyrrole Th(IV) phosphate at 30, 45 and 60 °C and that of polyaniline Sn(IV) phosphate at 25, 35 and 45 °C followed adequately a Freundlich adsorption behavior and can be represented by the equation:

$$x/m = KC^{1/n} \quad \ldots\ldots (1)$$

In case of adsorption on polypyrrole Th(IV) phosphate, x/m is the surface concentration of trichloroacetic acid in m moles per gram of the exchanger represented as Cs, C is the equilibrium concentration of trichloroacetic acid in m moles represented as Ce, and K and 1/n are constants.

While for polyaniline Sn(IV) phosphate, x/m is the surface concentration of mancozeb in m moles per gram of the exchanger represented as Cs, C is the equilibrium concentration of mancozeb (m mol ml^{-1}) represented as Ce, and K and 1/n are constants.

According to this equation plots of log Ce versus log Cs for polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate are straight lines at desirable temperatures (Fig. 6.5 and Fig. 6.6), and K and 1/n are the constants determined from the intercepts and slopes of the starting lines, respectively, fitted to the points by the least squares method. The values obtained are listed in Table 6.5 and Table 6.6.

Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constant K_o (or the thermodynamic coefficient) with the

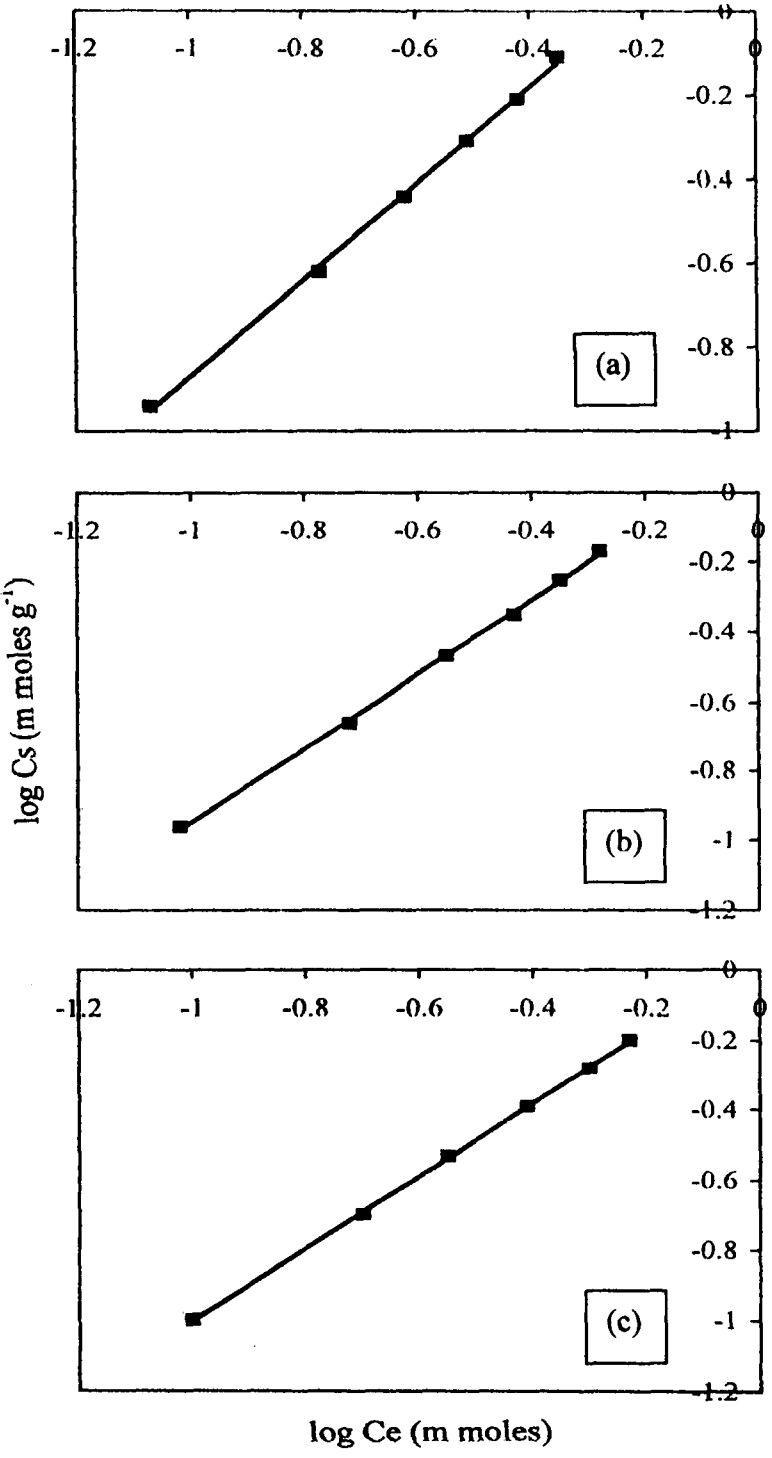

Fig. 6.5. Freundlich isotherm of trichloroacetic acid adsorption on polypyrrole Th(IV) phosphate at 30 °C (a), 45 °C (b) and 60 °C (c).

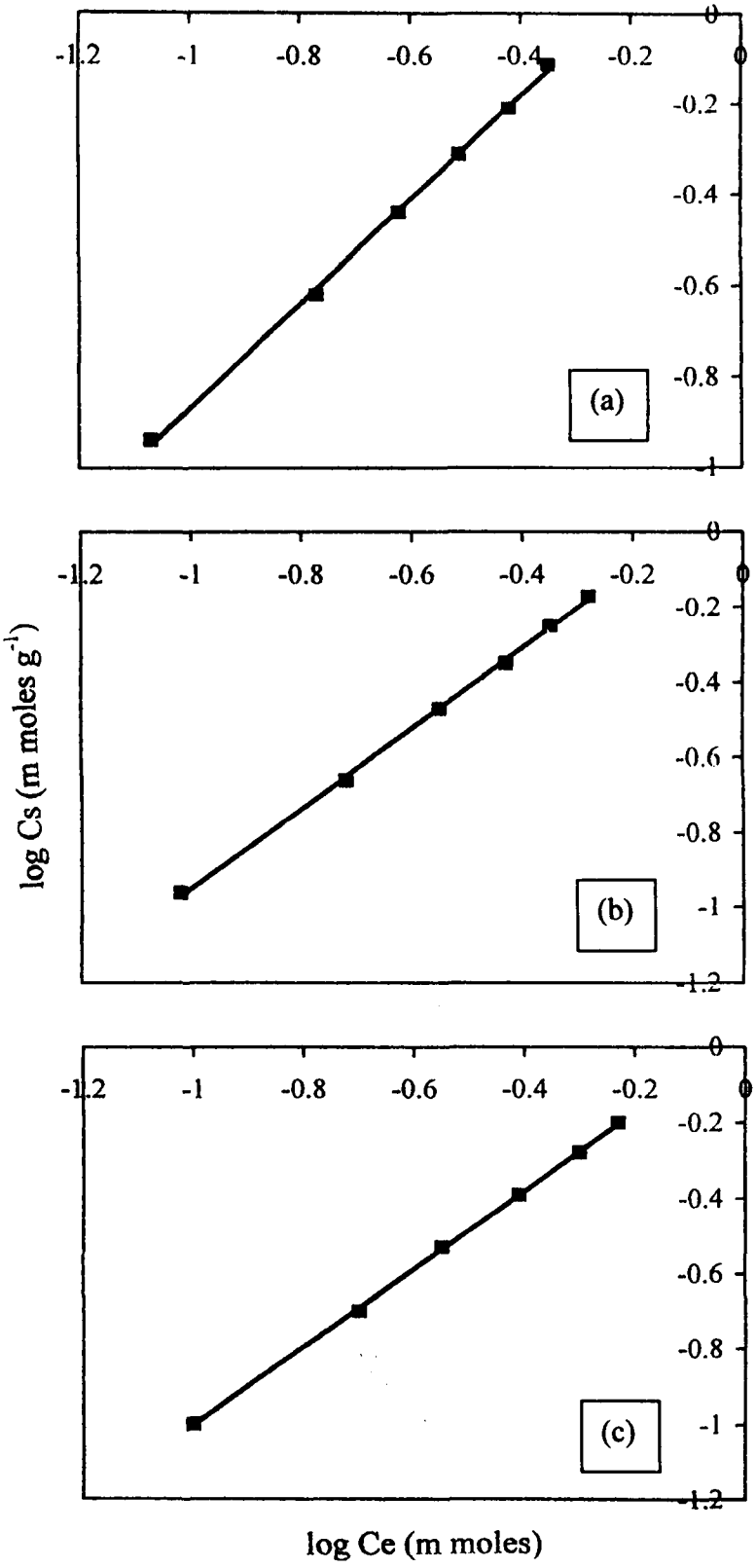

Fig. 6.6. Freundlich isotherm of mancozeb adsorption on polyaniline Sn(IV) phosphate at 25 °C (a), 35 °C (b) and 45 °C (c).

Table 6.5

Freundlich isotherm constants K and 1/n for the adsorption of trichloroacetic acid on polypyrrole Th(IV) phosphate composite cation-exchanger

Freundlich Constant	Temperature (°C)		
	30	45	60
K	0.2767	0.1187	0.355
1/n	1.1472	1.0663	0.0387

Table 6.6

Freundlich isotherm constants K and 1/n for the adsorption of mancozeb on polyaniline Sn(IV) phosphate composite cation-exchanger

Freundlich Constant	Temperature (°C)		
	25	35	45
K	0.82	0.57	0.85
1/n	1.58	1.51	1.67

change in temperature. The constant, K_o for the adsorption reaction can be defined as follows:

$$K_o = \frac{a_s}{a_c} = \frac{v_s C_s}{v_s C_e} \qquad \ldots\ldots (2)$$

where a_s is the activity of adsorbed solute, a_e is the activity of the solute in solution at equilibrium, C_s is the surface concentration of trichloroacetic acid and mancozeb in m mol per gram of exchanger, C_e is the concentration of trichloroacetic acid and mancozeb at equilibrium (m mol ml^{-1}), ν_s is the activity coefficient of the adsorbed solute and ν_e is the activity coefficient of the solute in solution.

As the concentration of the solute in the solution approaches zero, the activity coefficient approaches unity, reducing Eq. 2 to the following form-

$$K_o = \frac{a_s}{a_e} = \frac{C_s}{C_e} \qquad \ldots\ldots (3)$$

Values of K_o are obtained by plotting ln (C_s/C_e) versus C_s (Fig. 6.7 and Fig. 6.8) and extrapolating C_s to zero [19]. The straight line obtained is fitted to the points based on a least squares analysis. Its intercept with the vertical axis gives the values of K_o. Standard free energy changes ($\Delta G°$) for interactions are calculated [29] from the relationship:

$$\Delta G° = - RT \ln K_o \qquad \ldots\ldots (4)$$

where R is the universal gas constant and T is the temperature in Kelvin. The average standard enthalpy change ($\Delta H°$) is then calculated from the well-known Van't Hoff equation:

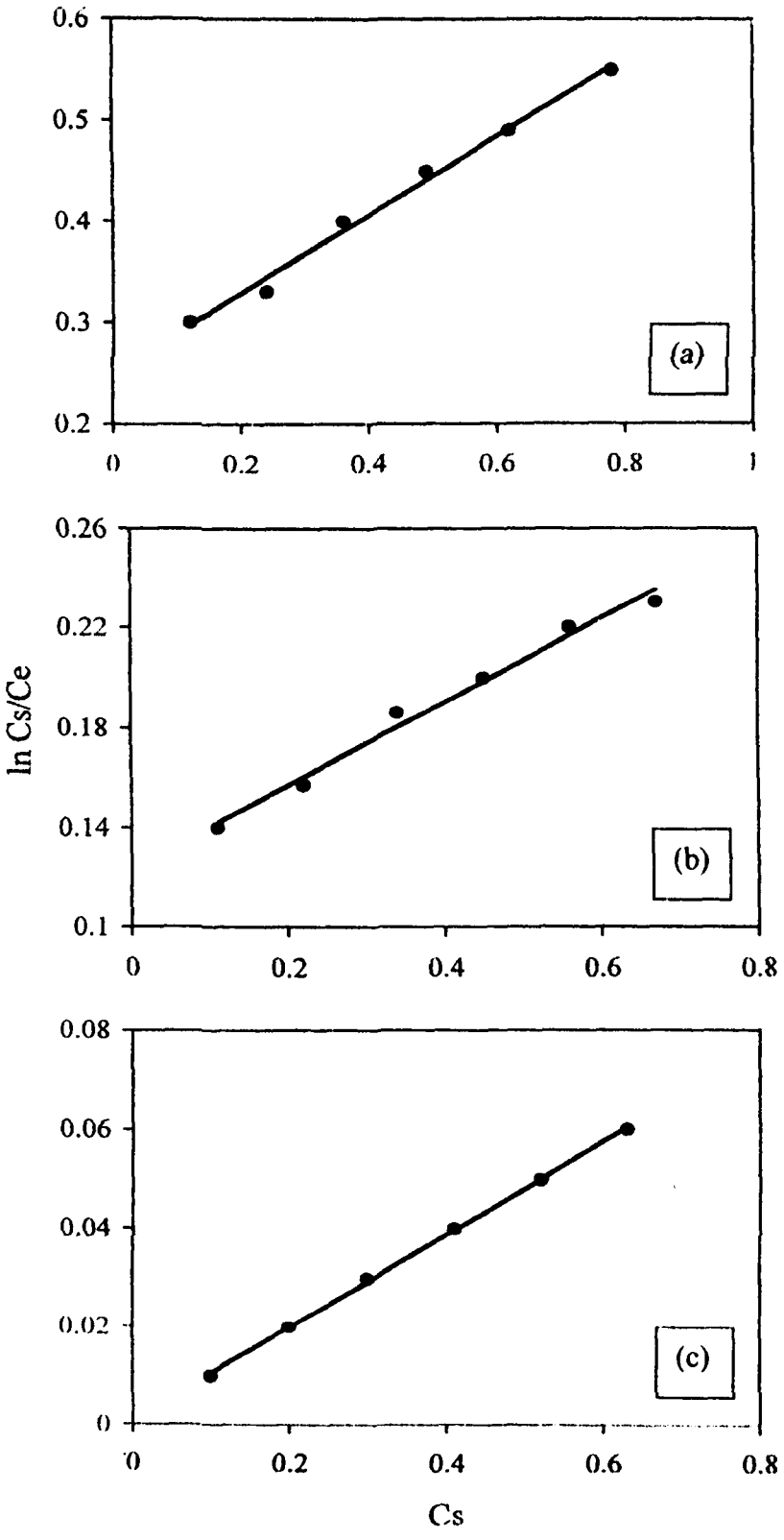

Fig. 6.7. Plots of ln Cs/Ce versus Cs on polypyrrole Th(IV) phosphate composite cation-exchanger at 30 °C (a), 45 °C (b) and 60 °C (c).

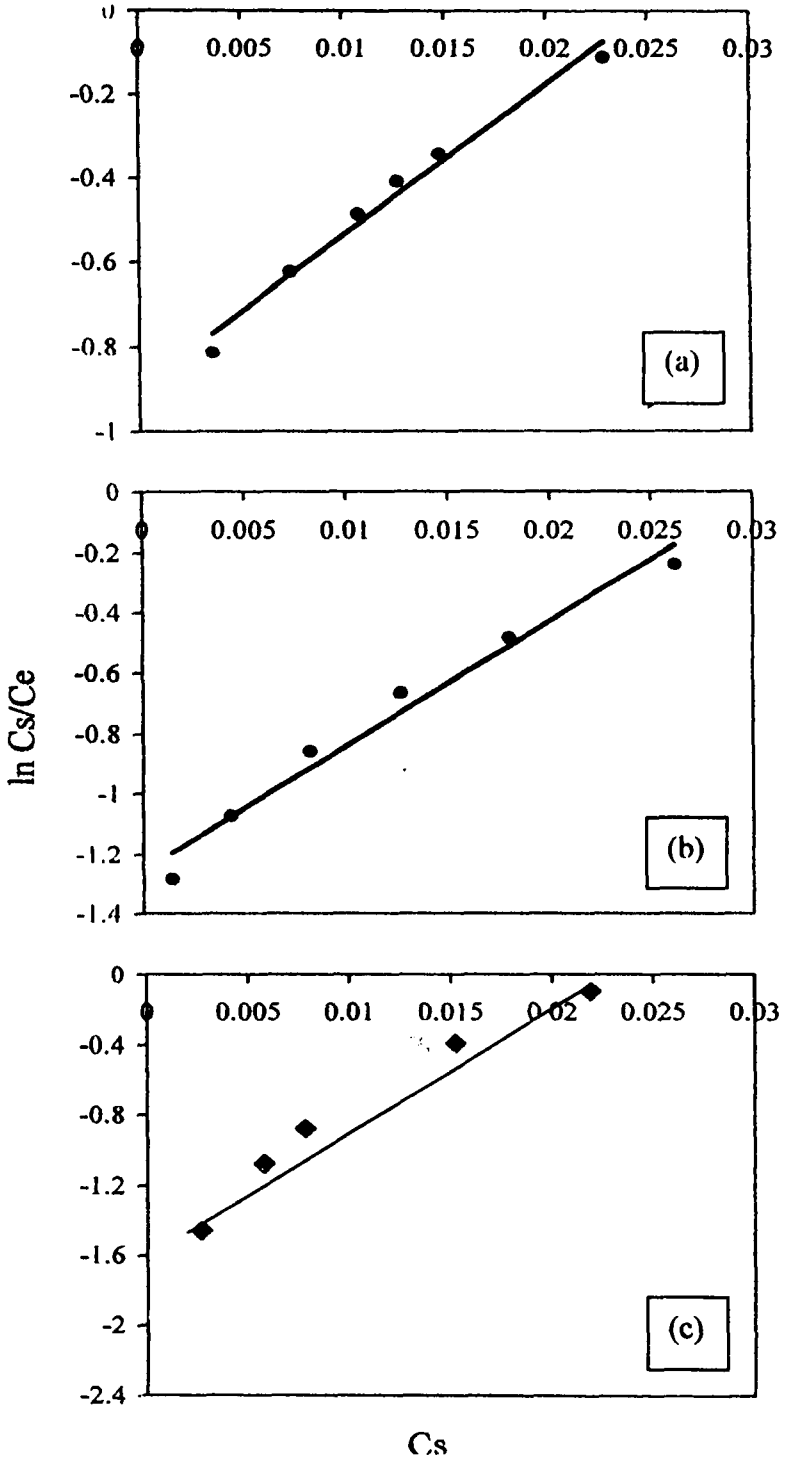

Fig. 6.8. Plots of ln Cs/Ce versus Cs on polyaniline Sn(IV) phosphate composite cation-exchanger at 25 °C (a), 35 °C (b) and 45 °C (c).

$$\ln K_o(T_3) - \ln K_o(T_1) = \frac{-\Delta H^{\circ}\ (T_1 \text{ to } T_3)}{R} \left(\frac{1}{T_3} - \frac{1}{T_1}\right) \quad \ldots\ldots (5)$$

where T_3 and T_1 are two different temperatures. Standard entropy changes ($\Delta S°$) are calculated using the equation-

$$\Delta G° = \Delta H° - T\Delta S° \quad \ldots\ldots (6)$$

The thermodynamic parameters obtained for the absorption trichloroacetic acid and mancozeb on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate cation-exchangers, respectively are given in Table 6.7 and Table 6.8. The negative values of the standard enthalpy change ($\Delta H°$) in both cases indicate the exothermic nature of the adsorption process [30]. It is supported by the adsorption of trichloroacetic acid and mancozeb decreases with the increase in temperature. The negative values of ($\Delta S°$) for trichloroacetic acid and mancozeb adsorption indicate the decrease of the degree of randomness at the surface of the polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate, respectively. This decreasing in the randomness lead to an increase in the adsorption capacity for trichloroacetic acid and mancozeb on polypyrrole Th(IV) phosphate and polyaniline Sn(IV) phosphate, respectively.

Table 6.7

Values of various thermodynamic parameters for the adsorption of trichloroacetic acid on polypyrrole Th(IV) phosphate composite cation-exchanger

Thermodynamic constant	Temperature (°C)		
	30	45	60
K_o	0.2509	0.1214	0.0011
$\Delta G°$ (K cal mol^{-1})	0.8448	1.3302	4.5
$\Delta H°$ (K cal mol^{-1})	- 44.88	- 44.88	- 44.88
$\Delta S°$ (K cal mol^{-1} deg^{-1})	$- 1.485 \times 10^{-1}$	$- 1.453 \times 10^{-1}$	$- 1.482 \times 10^{-1}$

Table 6.8

Values of various thermodynamic parameters for the adsorption of mancozeb on polyaniline Sn(IV) phosphate composite cation-exchanger

Thermodynamic constant	Temperature (°C)		
	25	35	45
K_o	1.2536	1.2534	1.1963
$\Delta G°$ (K cal mol^{-1})	- 0.1336	- 0.1380	- 0.1131
$\Delta H°$ (K cal mol^{-1})	- 0.58	- 0.58	- 0.58
$\Delta S°$ (K cal mol^{-1} deg^{-1})	2.3551×10^{-3}	1.4351×10^{-3}	$- 1.4682 \times 10^{-3}$

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Appendix

Appendix - I

List of Abstracts Published in Seminars and Conferences

1. Separation and determination of toxic heavy metal pollutant Pb(II) from industrial waste effluents and ground water by a new and novel polymeric-inorganic composite type fibrous material 'polypyrrole Th(IV) phosphate' used as a cation-exchanger and Pb(II) ion-selective membrane electrode.

   M. M. Alam, Inamuddin and A. A. Khan*
   Third International Conference on Surface Science and Catalysis; December 8-9, 2003, Ajmer, India.

2. Organic-inorganic composite fibrous type material "polypyrrole Th(IV) phosphate" used as a cation-exchanger and Pb(II) ion-selective electrode for separation and determination of heavy toxic metal pollutant Pb(II) from industrial waste effluents and ground water.

   Inamuddin, M. M. Alam and A. A. Khan*
   A seminar on Environmental vision: retrospect and Prospect: February 28, 2004, Etawah, U.P. India.

3. Preparation, characterization and analytical applications of polyaniline Sn(IV) phosphate, a polymeric-inorganic composite cation-exchange material

   Asif Ali Khan*, and Inamuddin
   Second International Symposium on the Separation and Characterization of Natural and Synthetic Macromolecules (SCM-2)", on February 2nd - 4th, 2005 in Amsterdam (The Netherlands).

4. Adsorption of carboxylic acid and their derivatives on activated charcoal in water.

   A. A. Khan*, Inamuddin and M.M. Alam; International Activated Carbon Conference, September 25-26, 2003, Pittsburgh, Pennsylvania, U.S.A.

Appendix - II

Reprints of Research Papers

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Materials Research Bulletin 40 (2005) 289–305
Materials Research Bulletin
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Preparation, characterization and analytical applications of a new and novel electrically conducting fibrous type polymeric–inorganic composite material: polypyrrole Th(IV) phosphate used as a cation-exchanger and Pb(II) ion-selective membrane electrode

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Abstract

'Polymeric–inorganic' composite type of cation-exchanger 'polypyrrole Th(IV) phosphate' was prepared by mixing polypyrrole into fibrous inorganic precipitate of Th(IV) phosphate. This type of composite possesses a new class of hybrid ion-exchangers with good ion-exchange capacity (I.E.C.), higher stability, reproducibility and selectivity for heavy metals. The physicochemical properties of the material were determined using AAS, CHN elemental analysis, ICP-MS, UV-VIS spectrophotometry, FTIR, thermogravimetric analyses-differential thermal analysis (TGA-DTA), XRD and SEM studies. Ion-exchange capacity, pH-titrations, elution and distribution behavior etc. were also carried out to characterize the material. On the basis of distribution studies, the material was found to be highly selective for Pb(II), a heavy metal pollutant in the environment. Its selectivity was examined by achieving some important binary separations like Pb(II)–Zn(II), Pb(II)–Ni(II), Pb(II)–Cu(II) and Pb(II)–Cd(II) on its column that indicate its utility in environmental pollution control in one-way or other. This electroactive material also showed the DC electrical conductivity in the range of 10^{-6} to 10^{-4} S cm^{-1}. A new heterogeneous precipitate based selective ion-sensitive membrane electrode was developed by using this composite cation-exchanger for the determination of Pb(II) ions in solutions. The analytical utility of this electrode was established by employing it as an indicator electrode in electrometric titrations.

Keyword: B. Chemical synthesis

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1. Introduction

Composite materials formed by mixing organic polymers and inorganic particles; possess all the good properties of both the constituents and an enhanced utility thereof. The combination of organic and inorganic precursors yields hybrid materials that have mechanical properties not present in the pure materials. The organic group can be reactive which implies that it is able to form an organic network as well as inorganic network. In designing composite materials scientists and engineers have ingeniously combined various metals, ceramics, and polymers to produce a new generation of extraordinary materials that encompass a wide variety of applications. Most composites have been created to improve combination of mechanical characteristics such as stiffness, toughness, and ambient and high temperature strength. Of particular interest is the molecular level combination of two different components that may lead to new composite materials that are expected to provide many possibilities termed 'organic-inorganic hybrid' materials.

This type of hybrid composites prepared with electrically conducting polymers have emerged as fascinating materials due to a wide range of other desirable properties such as architectural flexibility, environmental stability, ease of fabrication, light weight, mechanical property and so on. Therefore, these materials are finding applications from coating to lubricants to solid-state technology to biotechnology. Conducting polymers possess good tuneable electrical conductivity and are organic electrochromic materials with chemically active surface [1,2]. But they are chemically sensitive and have poor mechanical properties and thus pose a processibility problem. On the other hand, inorganic oxides or metal acid salts show the presence of more sites for surface reactivity and are highly porous in sol form. The metal oxides constitute a class of compounds widely used as cathode material in Li-ion batteries [3]. They also have good mechanical properties and are good dispersants too [4]. Thus composite materials formed through the incorporation of inorganic materials and organic polymers are attracted for the purpose of creating high performance or high functional polymeric materials. Recently, several groups have combined conductive polymers with metal oxides to generate hybrid composites that possess higher reversible capacity, redox cyclability and structural stability [5–9]. The properties of composites of such kind are strongly dependent on concentration of polymer. Polypyrrole, one of the conducting polymers, has received lot of attention in the preparation of composites due to its high stability in conducting oxidized form [10–14].

The synthesis of polymeric–inorganic composite has received a great deal of attention because it provided new material with special mechanical, chemical, electrochemical, and optical as well as magnetic properties. In literature, various methods of preparing these hybrid materials have been reported [15–19]. The conversion of inorganic ion-exchangers has been taking place into composite ion-exchange materials is the latest development in this discipline. These materials are used in the general areas of chemical sensors, chromatography, fabrication of selective materials, and electrical and electronic applications. Efforts have been made to improve the chemical, mechanical and thermal stabilities of ion-exchangers and to make them high selective for certain heavy metal ions. Inorganic precipitate ion-exchanger based on organic polymeric matrix must be an interesting material, as it should possess the mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger regarding its selectivity towards some particular metal ions. It was therefore considered to synthesize such hybrid ion-exchanger with a good ion-exchange capacity (I.E.C.), high stabilities, reproducibility, and selectivity for heavy metal ions, indicating its environmental applications. In this paper, we report the preparation of composite of conducting polymer,

polypyrrole and inorganic precipitate, Th(IV) phosphate by a process of simultaneous gelation of inorganic acid salt as well as polymerization of pyrrole monomer using different amounts of monomer in different volume of inorganic precipitates. This material was characterized using various instrumental and non-instrumental techniques.

Precipitate based ion-selective membrane electrodes are well known as they are successfully employed for determination of several anions and cations [20]. The heterogeneous precipitate ion-exchange membrane obtained by embedding ion-exchangers as electroactive material in the polymer binder i.e. epoxy resin (araldite or polystyrene or PVC) have been extensively employed as potentimetric sensors such as chemical sensors, ion sensors, or more commonly ion-selective membrane electrodes, gas sensors etc. [21–35]. An attempt has also been made to obtain ion-exchanger based membrane electrode using the proposed composite cation-exchange material as an electroactive component which can be utilized for the selective determination of heavy metal ions, Pb(II) in the solution.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, GSC, E-merck (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), FTIR spectrophotometer (Perkin-Elmer Spectrum-BX, U.S.A.), an automatic thermal analyzer (V2.2A Du Pont 9900), a PW 1148/89 based X-ray diffractometer (Phillips, Holland), an elemental analyzer (Carlo-Erba 1180), a double beam atomic absorption spectrophotometer (GBC 902, Australia), an inductively coupled plasma mass spectrophotometer, an electron microscope (LEO 435 VP, Australia) with attached imaging device, a digital Flame photometer (Elico CL 22D, India), a UV–vis spectrophotometer (Elico EI 301E, India), a water bath incubator shaker. A four-in-line probe electrical conductivity-measuring instrument (Scientific Equipment, India) and a digital potentiometer (Equiptronics EQ 609, India) with saturated calomel electrode as reference electrode were used.

2.2. Preparation of reagents

Solution (0.1 M) of thorium nitrate, $Th(NO_3)_4 \cdot 5H_2O$ was prepared in 1 M HNO_3 while orthophosphoric acid, H_3PO_4 solutions of different molarities and 0.1 M $FeCl_3$ solution were prepared in demineralized water (DMW). Pyrrole solution of 33.33% concentration (v/v) was prepared in toluene.

2.3. Preparation of Th(IV) phosphate

The inorganic precipitates of Th(IV) phosphate were synthesized as reported earlier [36] by mixing a solution of 0.1 M $Th(NO_3)_4 \cdot 5H_2O$ in 1 M HNO_3 at the flow rate at 0.5 ml min^{-1} to a solution of H_3PO_4 in different molarities. Constant stirring was done during mixing using a magnetic stirrer at a temperature of 85 ± 5 °C, white gel type slurries were obtained. After digestion of the mixture for several hours, it was cooled to room temperature in each case.

2.4. Preparation of polypyrrole Th(IV) phosphate

$FeCl_3$ solution (0.1 M) was mixed thoroughly with the inorganic precipitate of Th(IV) phosphate, to which approximately 33.33% solution of pyrrole in toluene was added drop wise, continuous stirring was done during the addition of pyrrole solution, slowly the white inorganic precipitate gel turned first to green and then to black. The reaction mixture was kept for 24 h under ambient condition (25 ± 2 °C).

Now the polypyrrole based composite gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ferric chloride. The washed gels then dried over P_4O_{10} at 30 °C in an oven. The dried products were immersed in DMW to obtain small granules. They were converted to the H^+-form by keeping it in 1 M HNO_3 solution for 24 h with occasional shaking intermittently replacing the supernatant liquid with a fresh acid. The excess acid was removed after several washings with DMW. The materials were finally dried at 40 °C and sieving to obtain particles of particular size range (~125 μm). Hence a number of polypyrrole Th(IV) phosphate composite samples were prepared (Table 1) and on the basis of Na^+ ion-exchange capacity, percentage of yield and physical appearances, sample S-5 was selected for further studies.

2.5. Chemical composition

To determine the chemical composition of polypyrrole Th(IV) phosphate (sample S-5), two hundred mg of the sample was dissolved in 20 ml of concentrate H_2SO_4. The material was analysed for 'thorium(IV)' by ICP-MS and phosphate by the phosphovanado molybdate method [37]. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The weight percent composition of the material was: Th, 30.793; P, 9.622; C, 18.794; H, 3.340; N, 5.080; O, 32.371.

2.6. Chemical dissolution

Two hundred mg portions of the sample (S-5) were treated with 20 ml each of different acids, bases, organic solvents etc. for 24 h with intermittent shaking. The supernatant liquid was analyzed for Th(IV) by ICP-MS while phosphate was determined as usual by the phosphovanado molybdate method [37]. The results are summarized in Table 2.

2.7. Thermal treatment

Samples (1 g) of the cation-exchanger in H^+ form were heated at various temperatures in a muffle furnace for 1 h each and the Na^+ ion exchange capacities were determined after cooling them at room temperature. The results are shown in Table 3.

2.8. Thermogravimetric analyses-differential thermal analysis (TGA-DTA) studies

Simultaneous TGA-DTA studies were also carried out on heating the sample material S-5 (as-prepared) up to 900 °C at a constant rate (~10 °C min^{-1}) in the air atmosphere. Fig. 1 shows the TGA-DTA curves of the cation-exchange material.

Table 1
Conditions of preparation and the ion-exchange capacity of polypyrrole Th(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratio (v/v)					Appearance of the beads after drying	Na^+ ion exchange capacity (meq dry g^{-1})
	0.1 M $Th(NO_3)_4.5H_2O$ in 1 M HNO_3	H_3PO_4	Digestion time (h)	$FeCl_3$ (0.1 M)	Pyrrole in toluene (33.33%)		
S-1	5	2 (1 M)	4	2	0.30	Blackish granular	1.19
S-2	5	2 (1 M)	24	2	0.30	Blackish granular	0.78
S-3	5	3 (1 M)	4.30	2	0.30	Blackish granular	1.10
S-4	5	2 (2 M)	24	2	0.30	Blackish granular	0.62
S-5	5	2 (2 M)	5	2	0.30	Blackish granular	1.56
S-6	5	2 (2 M)	5	–	–	White sheet	0.72
S-7	–	–	–	2	0.30	Black powder	0.05
S-8	5	2 (2 M)	5	2	0.18	Blackish granular	0.58
S-9	5	2 (2 M)	5	2.5	0.42	Blackish granular	0.27
S-10	5	2 (2 M)	5	2.5	0.60	Blackish granular	0.29
S-11	5	2 (2 M)	5	2.5	0.75	Blackish granular	0.51
S-12	5	2 (2 M)	5	2.5	0.90	Blackish granular	0.31

Table 2
Chemical stability of polypyrrole Th(IV) phosphate in various solvents

Solvent used (20 ml)	Amount dissolved (mg/20 ml)	
	Th(IV)	Phosphorus
DMW	0.00	0.25
1 M HCl	0.12	1.88
2 M HCl	0.35	2.62
4 M HCl	Completely dissolved	
1 M HNO_3	0.27	1.55
2 M HNO_3	0.69	3.12
4 M HNO_3	Completely dissolved	
0.5 M H_2SO_4	0.93	7.54
2 M H_2SO_4	Completely dissolved	
1 M $HClO_4$	0.23	2.02
2 M $HClO_4$	0.62	3.55
4 M $HClO_4$	Completely dissolved	
0.1 M KOH	0.07	1.04
0.1 M NaOH	0.06	0.84
1 M NH_4OH	0.04	1.50
1 M $NaNO_3$	0.00	0.38
10% Dimethylsulphoxide (DMSO)	0.00	0.21
Acetone	0.00	0.22
n-Butyl alcohol	0.01	0.45

Table 3
Effect of temperature on ion-exchange capacity of polypyrrole Th(IV) phosphate cation-exchanger on heating time for one hour

Heating temperature (°C)	Appearance (color)	Weight loss (%)	Na^+ ion-exchange capacity (meq dry g^{-1})	% Retention of I.E.C.
40	Blackish brown	–	1.56	100
100	Blackish brown	9.34	1.56	100
150	Blackish brown	12.15	1.56	100
200	Blackish brown	13.46	1.32	84.61
300	Black	19.26	0.96	61.54
350	Black	25.07	0.87	55.77
400	Black	30.80	0.45	28.85
500	Light gray	39.42	0.33	21.15
600	Light gray	43.91	0.22	14.10

2.9. FTIR studies

The FTIR spectrum of polypyrrole (S-7), Th(IV) phosphate (S-6) and polypyrrole Th(IV) phosphate (S-5) (as-prepared) dried at 50 °C was taken by KBr disc method and is given in Fig. 2.

2.10. X-ray studies

Powder X-ray diffraction pattern of the material S-5 (as-prepared) was recorded by a PW 1148/89 based diffractometer with Cu Kα radiation.

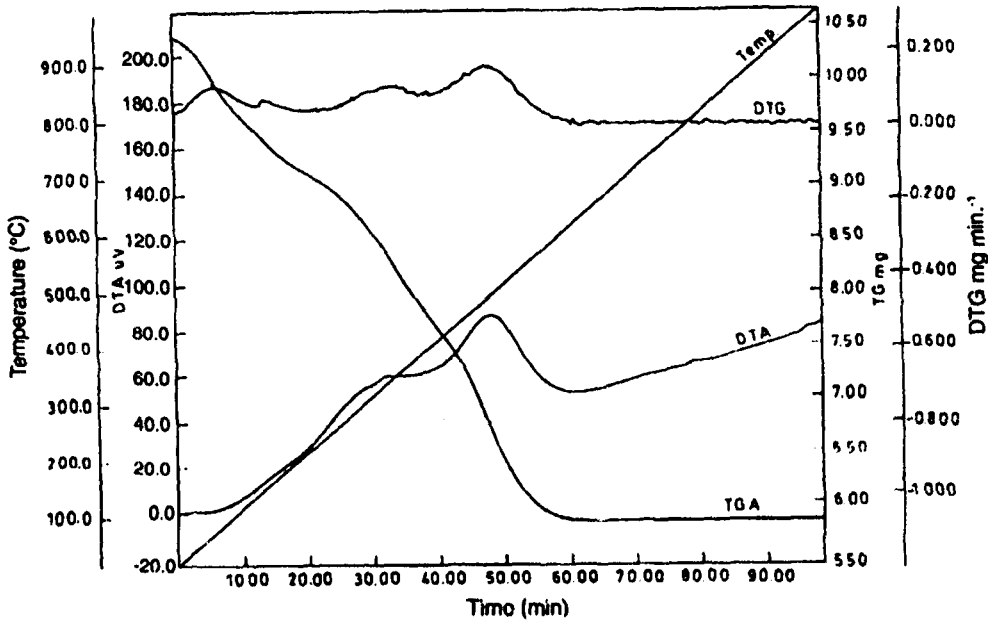


Fig. 1. Simultaneous TGA-DTA curves of polypyrrole Th(IV) phosphate (as-prepared).

2.11. Scanning electron microscopy (SEM) studies

SEM was performed on ground materials (as prepared) by an electron microscope at various magnifications. Fig. 3 presents the microphotographs of samples S-7, S-6 and S-5.

2.12. Electrical conductivity measurements

The composite ion-exchange material (S-5) was treated with 0.5 M aqueous HCl and washed for excess HCl with distilled water repeatedly till the filtrate gave a negative test for hydrogen ions. Then the material (0.5 g) was finally ground in a mortar pastel and pellet was made at room temperature with the help of a hydraulic pressure instrument at 25 kN pressure for 20 min. The thickness of pellet was measured by a micrometer.

Four probe DC electrical conductivity measurements with increasing temperature for the representative sample (S-5) (as prepared and HCl treated) were performed on pressed pellets by using a 4-in-line-probe DC electrical conductivity measuring technique. The sample to be tested is placed on the base plate of four-probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure is applied on the probes and then it was tighten in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply is then switched on, the temperature was allowed to increase gradually while current and voltage was recorded with rise in temperatures.

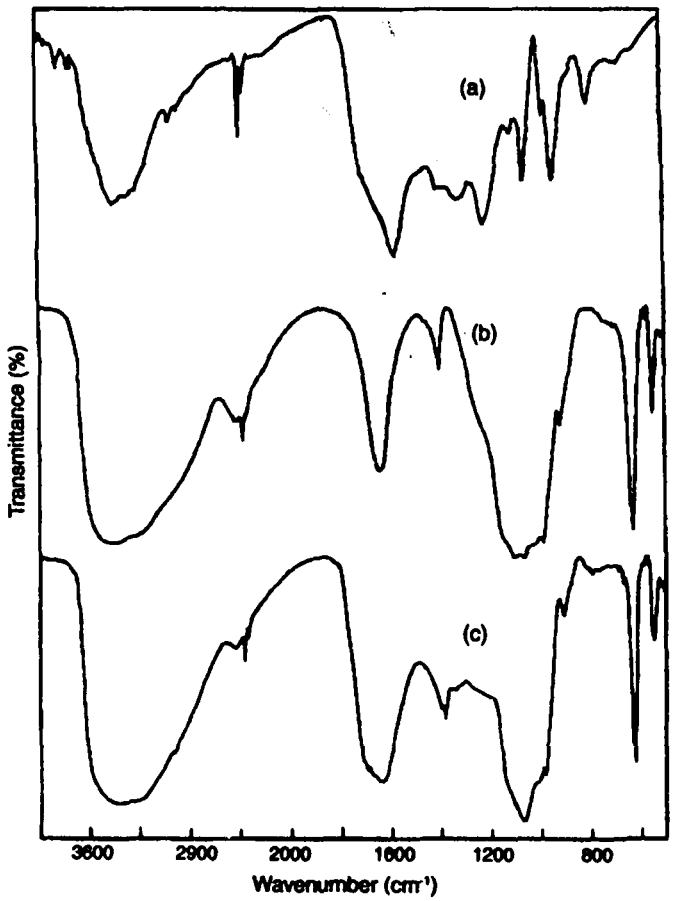


Fig. 2. FTIR spectra of as prepared polypyrrole (a), Th(IV) phosphate (b) and polypyrrole Th(IV) phosphate composite material (c).

2.13. Distribution (sorption) studies

The distribution coefficient (K_d values) of various metal ions on polypyrrole Th(IV) phosphate were determined by batch method in various solvents systems. Various 200 mg of the composite cation-exchanger beads (S-5) in the H^+ ion form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion concentration was to adjust that it did not exceed 3% of its total ion exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solution of EDTA [38] and some heavy metal ions such as [Pb^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution coefficient (K_d) values calculated using the formula given below:

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \text{ ml g}^{-1} \quad (1)$$

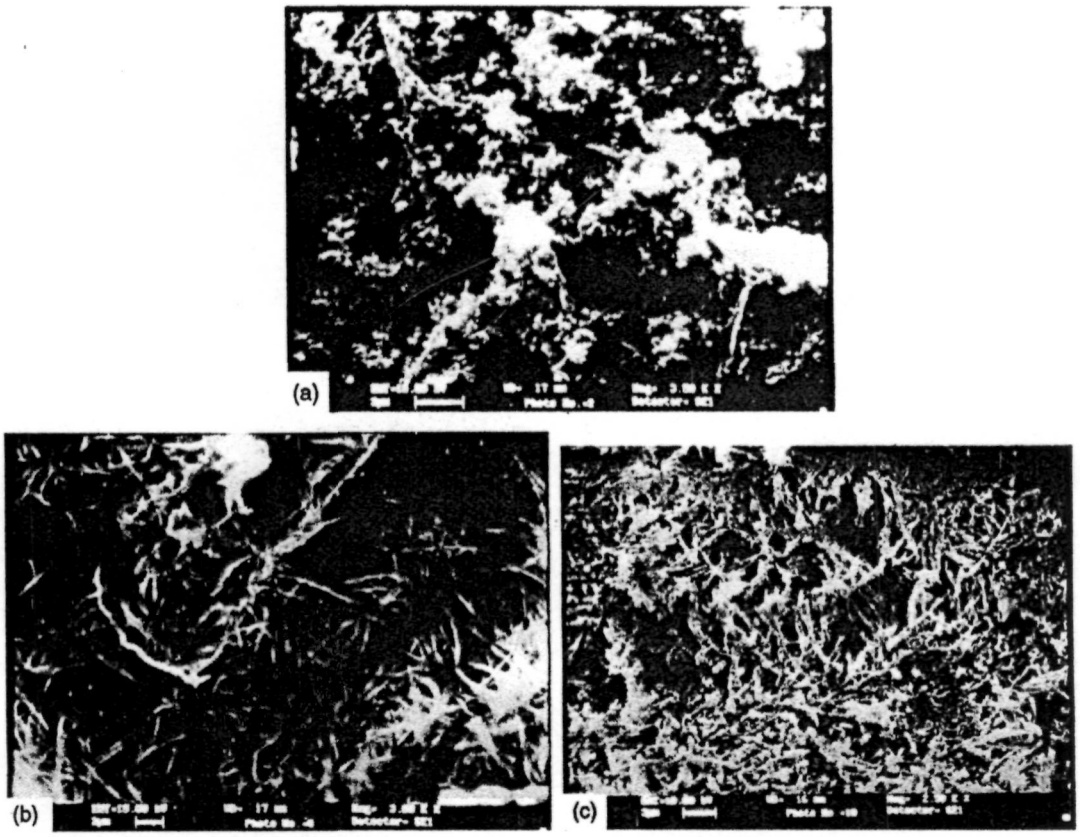


Fig. 3. Scanning electron microphotographs (SEM) of chemically prepared polypyrrole at the magnification of 3500× (a), Th(IV) phosphate at the magnification of 3000× and (b) and polypyrrole Th(IV) phosphate composite system at the magnification of 2500× (c).

where I is the initial amount of the metal ion in the solution phase, F final amount of metal ion in the solution phase. V is the volume of the solution (ml) and M the amount of exchanger (g).

2.14. Quantitative separation of metal ions

Quantitative binary separations of some important metal ions of analytical utility were achieved on polypyrrole Th(IV) phosphate column. One gram of the cation-exchanger, S-5 (~125 μm) in H^+-form were used for column separations in a glass tube having an internal diameter of ~0.6 cm and a height of 35 cm. The column was washed thoroughly with DMW and the mixture of two metal ions having initial concentrations of 0.01 M each, to be separated was loaded on it and allowed for one hour to absorb the metal ions on the exchanger and pass on to the column gently (maintaining a flow rate of two to three drops per minute) till the level was above the surface of the material. After recycling two or three times to ensure complete absorption of the mixture on column beads, the separation was achieved by passing a suitable solvent at a flow rate of 1 ml min^{-1} through the column as eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration.

2.15. Fabrication of ion-selective electrode

The fibrous type composite cation-exchanger, S-5 (100 mg) was ground to fine powder, and was mixed thoroughly with Araldite (Ciba-Geigy) (100 mg) on whatman's filter paper No. 42 and a master membrane of 0.42 mm thickness was prepared. A piece of membrane was cut out and fixed at one end of a pyrex glass tube (o.d. 0.8 cm, i.d. 0.6 cm) with Araldite. The tube was filled with 0.1 M lead nitrate. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE) | Internal electrolyte 0.1 M Pb^{2+} | Membrane | Sample solution | External reference electrode (SCE)

In advance of measurements of the electrode potential (at 25 ± 2 °C) for a series of standard solutions of $Pb(NO_3)_2$ (10^{-9} M–10^{-1} M). The membrane of the electrode was conditioned by soaking in 0.1 M $Pb(NO_3)_2$ solution for 5–7 days and for 1 h at least before use. In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time and working pH range.

3. Results and discussions

In this work, various samples of new and novel polypyrrole based 'organic-inorganic' electrically semiconducting fibrous type composite ion-exchange materials were developed by incorporating polypyrrole into inorganic matrices of fibrous Th(IV) phosphate. Among them sample S-5 (Table 1) possessed good yield, better ion-exchange capacity and both chemical and thermal stabilities. However, sample S-5 of polypyrrole Th(IV) phosphate exhibited granulometric and mechanical properties, showing a good reproducible behavior as is evident from the fact that these materials obtained from various batches did not show any appreciable deviation in their percentage of yield and ion-exchange capacities. It was also found that the values of H^+ adsorption and H^+ liberation capacities are in close agreement. This material possessed a better Na^+ exchange capacity (1.56 meq g^{-1}) as compared to Th(IV) phosphate (0.72 meq g^{-1}).

The solubility experiment (Table 2) showed that the material has reasonable good chemical stability as the results indicated that the material was resistant to 2 M HCl, 2 M HNO_3, and 0.5 M H_2SO_4. This material is completely dissolved in 4 M HCl, 4 M HNO_3, 4 M $HClO_4$, and 2 M H_2SO_4. The chemical dissolution in DMW, alkaline media, $NaNO_3$, NH_3, DMSO, acetone and *n*-butyl alcohol was almost negligible. The chemical stability may be due to the presence of binding polymer, which can prevent the dissolution of heteropolyacids sols or leaching of any constituent element into the solution.

On heating at different temperatures for one hour, the mass, physical appearance and ion-exchange capacity of the dried sample material (S-5) were changed as the temperature increased as shown in Table 3. The material was found to possess higher thermal stability as the sample maintained about 69% of the initial mass by heating up to 400 °C. However, in respect to ion-exchange capacity, this material is found stable up to 150 °C and it remains about 56 percent of the initial ion-exchange capacity by heating up to 350 °C.

The TGA-DTA curve (Fig. 1) of the material showed continuous weight loss of mass (about 12%) up to 174 °C, which may due to removal of external water molecule [39]. Slow weight loss observed between 174 and 319 °C (may be due to the condensation of phosphate group) to pyrophosphate groups.

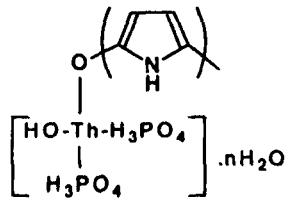
Further weight loss between 319 and 645 °C may be due to complete decomposition of the organic part of the material. At 645 °C onwards, a smooth horizontal section which represents the complete formation of the oxide form of the material. These transformations have also been supported by differential thermal analysis (DTA). The DTA curve indicates two exothermic peaks with maxima at 326 °C and 497 °C that also confirm the structural transformation in the material.

The FTIR spectrum of the composite cation-exchanger, sample S-5 (Fig. 2c) indicates the presence of extra water molecule in addition to the –OH groups and metal oxides present internally in the material. In the spectrum a strong broad band around 3400 cm^{-1} found which could be attributed to –OH stretching frequency. The peak at the 1647 cm^{-1} may be due to interstitial water present in the composite material [40]. An assembly of three peaks at 980–1080 cm^{-1} may represent the presence of ionic phosphate groups [41] in the material. The additional band at about 1400 cm^{-1} can be ascribed to stretching vibration of C–N [42]. This indicates that the material contains considerable amount of pyrrole.

The molar ratio of Th, P, C, H, N, and O in the material was estimated to be 1:2.34: 11.77:25.36:2.73:15.21 which can suggest the following formula of the material:

$$[(ThO_2)(H_3PO_4)_2 \cdot (-C_4H_2NH-)_3] \cdot nH_2O$$

and its structure can be written as:



Assuming that only the external water molecules are lost, at 174 °C the ~12% weight loss of mass represented by TGA curve must be due to the loss of nH_2O. From the above structure the value of 'n' the external water molecules can be calculated using Alberti's equation [43]:

$$18n = \frac{X(M + 18n)}{100} \tag{2}$$

where X is the percent weight loss (~12%) the exchanger by heating up to 174 °C and $(M + 18n)$ is the molecular weight of the material. The calculations give ~5 for the external water molecule (n) per molecule of the cation-exchanger (sample S-5).

SEM photographs of polypyrrole, Th(IV) phosphate and polypyrrole Th(IV) phosphate obtained at different magnifications (Fig. 3) indicating the binding of inorganic ion-exchange material with organic polymer, i.e. polypyrrole. The SEM pictures showed the difference in surface morphology of organic polymer, inorganic precipitate and composite material. It has been revealed that after binding of polypyrrole with Th(IV) phosphate, the morphology has been changed. The X-ray powder diffraction pattern of this cation-exchanger (sample S-5, as-prepared) exhibited no peak in the spectrum that suggesting an amorphous nature of the composite material.

Electrical conductivities of the pellets of polypyrrole based Th(IV) phosphate composite material (S-5) were determined from the measurement of conductivity of the samples using the four-probe method of conductivity measurement for semiconductors. The current-voltage data so generated at increasing

temperatures for the determination of electrical conductivity of the composite sample were processed for calculation of electrical conductivity using the following equation:

$$\sigma = \frac{\sigma_0}{G_7(W/S)} \tag{3}$$

where σ is the electrical conductivity in S cm^{-1}, $G_7(W/S)$ the correction factor used for the case of non-conducting bottom surface and it is a function of W, thickness of the sample under test (cm) and S, probe spacing (cm); i.e.

$$G_7\left(\frac{W}{S}\right) = \left(\frac{2S}{W}\right)\log_e 2 \tag{4}$$

and

$$\sigma_0 = \frac{I}{(V \times 2\pi S)} \tag{5}$$

where I is the current (A) and V the voltage (V).

The variations of electrical conductivity (σ) of the composite samples by raising temperatures (between 35 and 200 °C) are carried out. On examination, it was observed that the electrical conductivity of the samples increase with the increase in temperature and the values lie in the order of 10^{-6} to 10^{-4} S cm^{-1}, i.e., in the semiconductor region. To determine the nature of dependence of electrical conductivity on temperature plots of log σ versus $1000/T$ (K) were drawn (Fig. 4) and they followed Arrhenius equation similar to other semiconductors [44].

In order to explore the potentiality of the composite cation-exchange material in the separation of metal ions, distribution studies for 11 metal ions were performed in seven solvent systems (Table 4). The distribution studies showed that the material was found to be the highly selective for Pb(II), which is a major polluting metal in the environment. The separation capacity of the material has been demonstrated by achieving some important binary separations such as Pb^{2+}–Zn^{2+}, Pb^{2+}–Cd^{2+}, Pb^{2+}–Cu^{2+} and Pb^{2+}–Ni^{2+}. Table 5 summarizing the salient features of these separations.

The heterogeneous precipitate Pb(II) ion-selective membrane electrode obtained from polypyrrole Th(IV) phosphate cation-exchanger material gives linear response (Fig. 5) in the given range of 1×10^{-1} to 5×10^{-6} M with a slope of 29.17 mV per decade change in Pb(II) ion concentration, the slope value is

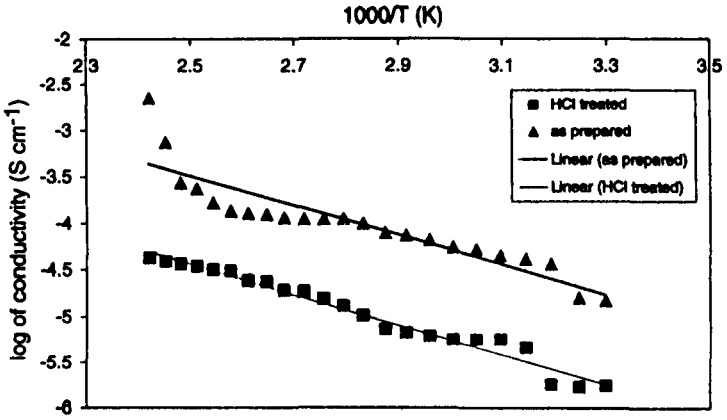


Fig. 4. Arrhenius plots for polypyrrole Th(IV) phosphate composite material.

Table 4
K_d values of some metal ions on polypyrrole Th(IV) phosphate (S-5) in different solvent systems

Metal ions	DMW	1×10^{-3} M $HClO_4$	1×10^{-2} M $HClO_4$	1×10^{-2} M HNO_3	1×10^{-1} M HNO_3	1×10^{-2} M HCl	1×10^{-1} M HCl
Cu^{2+}	233	133	29	11	5	24	6
Ni^{2+}	27	43	25	25	17	533	500
Pb^{2+}	900	2000	900	1900	300	600	90
Cd^{2+}	37	37	12	53	12	7	4
Mn^{2+}	70	43	28	33	26	23	17
Zn^{2+}	63	40	13	19	11	21	–
Hg^{2+}	1100	800	767	830	600	314	67
Co^{2+}	180	167	155	200	160	243	140
Bi^{3+}	20	40	133	120	25	120	400
Al^{3+}	20	40	133	120	25	120	400
Fe^{3+}	90	88	67	169	110	140	130

Table 5
Some binary separation of metal ions achieved on polypyrrole Th(IV) phosphate

Separation achieved	Amount loaded (μg)	Amount found (μg)	%Error	Eluent used	Volume of eluent (ml)
Zn(II)	1307.4	1294.33	−1.00	0.01 M HNO_3	50
Pb(II)	4144.0	4144.0	0.0	0.1 M $HClO_4$	60
Cd(II)	2248.0	2231.14	−0.75	0.01 M HNO_3	50
Pb(II)	4144.0	4092.2	−1.25	0.1 M $HClO_4$	60
Cu(II)	1271.0	1267.82	−2.5	0.01 M HNO_3	50
Pb(II)	4144.0	4216.52	+1.75	0.1 M $HClO_4$	60
Ni(II)	1174.2	1168.33	−0.5	0.01 M HNO_3	60
Pb(II)	4144.0	4175.08	+0.75	0.1 M $HClO_4$	60

close to Nerstian value, 29.6 mV/concentration decade for divalent cations. Below 5×10^{-6} M, a non-linear response was observed. A constant potential was obtained after 35 s and it was also observed the electrode potential remained unchanged with in the pH range of 3.0–8.5. The selectivity coefficients, $K^{POT}_{Pb.M}$ of different cations for the Pb(II) ion-selective polypyrrole Th(IV) phosphate electrode determined by the mixed solution method [45] were found to be less than unity. The selectivity coefficient indicates the extent to which a foreign ion (M^{n+}) interferes with the response of the electrode toward its primary ions. The results revealed that the electrode is selective for Pb(II) in presence of various interfering cations (Na^+, K^+, Cu^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+} etc.). The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometric titration of 0.01 M

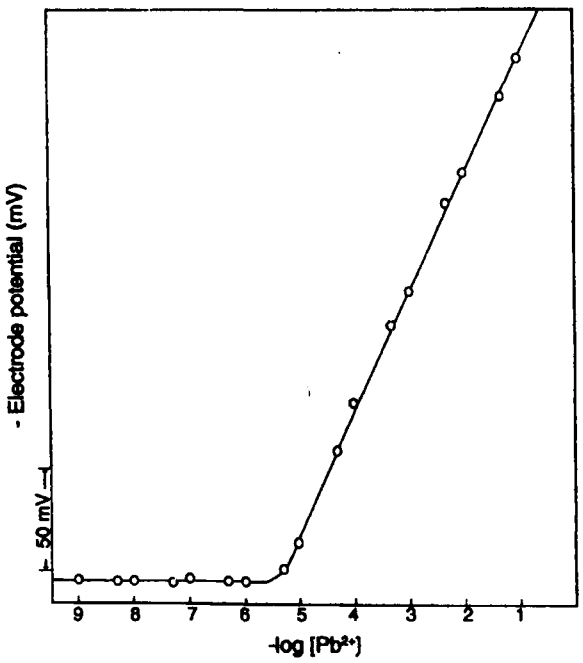


Fig. 5. Calbration curve for polypyrrole Th(IV) phosphate membrane electrode in aqueous solution of $Pb(NO_3)_2$.

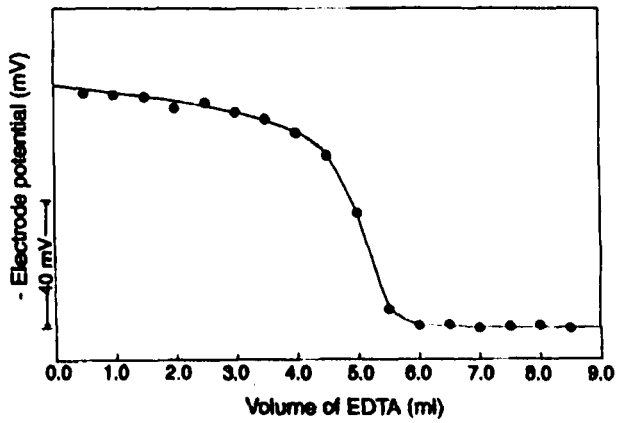


Fig. 6. Precipitation titration of Pb(II) against EDTA solution.

$Pb(NO_3)_2$ solution against 0.01 M EDTA solution. It was observed that a sharp rise in the titration curve occurs at the equivalence point (Fig. 6).

4. Conclusion

Fibrous ion-exchangers have been of recent origin and have a great advantage of having capability for obtaining in different forms such as conveyer belts, non-woven materials, staples, nets and clothes etc. This may open new and novel possibilities, of using these materials in environmental analysis. Thorium(IV) phosphate precipitate modified by incorporation of polypyrrole (a conducting polymer), was prepared in this study as a novel fibrous type 'polymeric–inorganic' composite cation-exchange material, has better ion-exchange capacity and is highly selective for lead. This adsorption behavior of this cation-exchanger is promising in the field of pollution chemistry where an effective separation method is needed for Pb(II) from other pollutants. It is evident from the results that the quantitative and efficient separations of various metal ions such as Pb(II) from Zn(II), Ni(II), Cu(II), Cd(II) etc. are feasible on polypyrrole Th(IV) phosphate column. Pb(II) sensitive membrane electrode was also developed which is chemically and mechanically stable and gives reproducible results with a useful lifetime, exhibiting a nearly Nernstian slope within functional pH range of 3.0–8.5. Further, the electrode can be used to determine Pb(II) ions in aqueous and non-aqueous media by both direct potentiometry and titration, and can successfully be used in determining Pb(II) ions in real samples.

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Determination and separation of Pb^{2+} from aqueous solutions using a fibrous type organic–inorganic hybrid cation-exchange material: Polypyrrole thorium(IV) phosphate

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Abstract

The separation of Pb^{2+} from aqueous solutions was studied using a fibrous type polypyrrole thorium(IV) phosphate cation-exchanger column. This type of organic–inorganic composite material was prepared by incorporating polypyrrole into inorganic precipitate of Th(IV) phosphate, providing a new class of hybrid cation-exchangers with good ion-exchange capacity, higher stability, reproducibility and selectivity for heavy metals. The physico-chemical properties of this material were determined using some instrumental analyses. Ion-exchange capacity, pH-titrations, elution and distribution behavior etc. were also carried out to understand the ion-exchange behavior of the material. On the basis of distribution studies, the material was found to be highly selective for Pb(II) and its selectivity was examined by achieving some important binary separations like Pb(II)–Zn(II), Pb(II)–Al(III), Pb(II)–Mg(II), Zn(II)–Hg(II) etc. on its column that indicate its utility in environmental pollution control in one-way or other. For the determination of Pb(II) ions in solutions, a new heterogeneous precipitate based selective ion-sensitive membrane electrode was developed by means of this composite cation-exchanger as electroactive material. The membrane electrode is mechanically stable, with a quick response time, and can be operated over a wide pH range. The selectivity coefficients were determined by mixed solution method and revealed that the electrode is selective for Pb(II) in presence of interfering cations. The practical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometric titration of Pb(II).

Keywords: Toxic element; Pb(II) separation; Organic–inorganic composite cation-exchanger; Polypyrrole Th(IV) phosphate; Pb(II) ion-selective membrane electrode; Potentiometric titrations

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1. Introduction

The organic inorganic hybrid materials should be considered as next generation composite materials that will encompass a wide variety of applications [1 14]. They can be used to modify organic polymer materials or to modify inorganic materials that exhibit very different properties from their original components [15–18]. In order to achieve stable materials with chromatographic properties interest has been generated in 'organic–inorganic' composite ion-exchange materials. Inorganic ion-exchanger based on organic polymeric matrix are interesting materials, as they possess mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger regarding its selectivity for some specific metal ions, indicating their useful environmental applications [19–28]. Efforts have been made to synthesize such hybrid ion-exchangers with a good ion-exchange capacity, high stability, reproducibility and selectivity for heavy toxic metal ions. A novel 'organic–inorganic' composite sample of polypyrrole Th(IV) phosphate has been synthesized in our laboratory that possessed such characteristics and high selectivity for lead, a hazardous toxic element in the environment.

Lead in the environment arises from both natural and anthropogenic sources. Generally, human exposure to lead comes from the following main sources: using leaded gasoline; using lead-based paint; having lead pipes in water supply systems; and exposure to industrial sources from processes such as lead mining, smelting, and coal combustion. Additional sources of lead include soldered seams in food cans, ceramic glazes, batteries, and cosmetics [29]. In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. Particularly, lead is toxic to the brain, kidneys, reproductive system, and cardiovascular system. Exposures can cause impairments in intellectual functioning, kidney damage, infertility, miscarriage, and hypertension [30]. Lead is a special hazard for young children. The utility of polypyrrole Th(IV) phosphate has been explored for the quantitative separation of Pb^{2+} from some binary mixtures on its column. Thus, an attempt has also been made to obtain ion-exchanger based membrane electrode using the proposed composite cation-exchange material as an electroactive component, which can be utilized for the selective determination of heavy metal ions, Pb(II) in the solution.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, GSC, E-merck (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), a double beam atomic absorption spectrophotometer (GBC 902, Australia), a digital Flame photometer (Elico CL 22D, India), a UV/vis spectrophotometer (Elico EI 301E, India), a water bath incubator shaker, a digital potentiometer (Equiptronics EQ 609, India) with saturated calomel electrode as reference electrode were used.

2.2. Preparation of polypyrrole thorium(IV) phosphate organic–inorganic composite material

The method of preparation of the inorganic precipitate of Th(IV) phosphate ion-exchanger was very similar to that of Alberti Constantino [31], with slight modification [32]. In this work, various samples of polypyrrole Th(IV) phosphate cation-exchanger was prepared when 0.1 M solution of $Th(NO_3)_4 \cdot 5H_2O$ in 1 M nitric acid solution was added at the flow rate of 0.5 ml min^{-1} to 1 M phosphoric acid solution prepared in DMW (demineralized water) in different molarities, at 85 ± 5 °C with constant stirring. White gel type slurries were obtained. After digestion for several hours it was cooled to room temperature. After this, 0.1 M $FeCl_3$ (ferric chloride) solution prepared in DMW were added drop wise, to which approximately 33.33% (v/v, in toluene) solution of pyrrole in different ratio's were mixed thoroughly with the inorganic precipitate of Th(IV) phosphate drop wise. Continuous stir-

Table 1
Ion-exchange capacity of various exchanging ions on polypyrrole Th(IV) phosphate cation-exchanger

Exchanging ions	pH of the metal solutions	Ionic radii (Å)	Hydrated ionic radii (Å)	I.E.C. (meq dry gm^{-1})	
				H^+-liberation	H^+-adsorption
Li^+	6.7	0.68	3.40	1.05	1.00
Na^+	6.7	0.97	2.76	1.56	1.29
K^+	6.8	1.33	2.32	1.21	1.22
Mg^{2+}	6.5	0.78	7.00	1.15	1.17
Ca^{2+}	6.5	1.06	6.30	1.38	1.35
Sr^{2+}	6.3	1.27	–	1.89	1.85
Ba^{2+}	6.3	1.43	5.90	2.74	2.75

ring was done during the addition of the pyrrole solution, slowly the white inorganic precipitate gel turned first green and then to black. The reaction mixtures were then kept for 24 h under ambient condition (25 ± 2 °C). Now these pyrrole based composite gels were filtered off; washed with DMW to remove excess acids and any adhering trace of ferric chloride. The washed gels then dried over P_4O_{10} at 30 °C in an oven. The dried products were immersed in DMW to obtain small granules. These were converted to the H^+-form by placing them in 1 M HNO_3 for 24 h with occasional shaking intermittently, replacing the supernatant liquid with a fresh acid. The excess acid was removed after several washings with DMW and again the material were dried at 40 °C and sieving to obtain particles of particular size range (~25 μm). Hence a number of polypyrrole Th(IV) phosphate composite samples were prepared and on the basis of Na^+ ion-exchange capacity (I.E.C.), percentage of yield and physical appearances, sample T-1 was selected for further studies. Conditions of preparation and the ion-exchange capacity of polypyrrole Th(IV) phosphate composite cation-exchange material (sample T-1) are given below:

After dissolving in concentrated H_2SO_4, the material was analyzed for 'thorium(IV)' by ICP-MS and phosphate by the phosphovanado molybdate method [33]. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The weight percent composition of the material was: Th, 30.793; P, 9.622; C, 18.794; H, 3.340; N, 5.080; O, 32.371.

2.3. Ion-exchange capacity (I.E.C.)

Polypyrrole Th(IV) phosphate is a cation-exchanger. The ion-exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation-exchanger was determined by standard column process. One gram (1 g) of the dry cation-exchanger, sample T-1 in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~ 1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1 M alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against

Sample	Mixing volume ratio (v/v)					Appearance of the beads after drying	Na^+ ion exchange capacity (meq dry gm^{-1})
	0.1 M $Th(NO_3)_4 \cdot 5H_2O$ in 1 M HNO_3	H_3PO_4	Digestion time (h)	$FeCl_3$ (0.1 M)	Pyrrole in toluene (33.33%)		
T-1	5	2 (2 M)	5	2	0.30	Blackish granular	1.56

a standard (0.1 M) NaOH solution using phenolphthalein indicator and the ion-exchange capacities (I.E.C.) in meq g^{-1} are given in Table 1.

2.4. Thermal effect on ion-exchange capacity (I.E.C.)

To study the effect of drying temperature on the I.E.C., 1 g samples of the composite cation-exchange materials (T-1) in the H^+-form were heated at various temperatures in a muffle furnace for 1 h and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature (Table 2).

Table 2
Effect of temperature on ion-exchange capacity of polypyrrole Th(IV) phosphate cation-exchanger on heating time for 1 h

Heating temperature (°C)	Appearance (color)	Na^+ ion-exchange capacity (meq dry gm^{-1})	% retention of I.E.C.
40	Blackish brown	1.56	100
100	Blackish brown	1.56	100
150	Blackish brown	1.56	100
200	Blackish brown	1.32	84.61
300	Black	0.96	61.54
350	Black	0.87	55.77
400	Black	0.45	28.85
500	Light gray	0.33	21.15
600	Light gray	0.22	14.10

2.5. Effect of eluant concentration

To find out the optimum concentration of the eluant for complete elution of H^+ ions, a fixed volume (250 ml) of $NaNO_3$ solution of varying concentrations were passed through a column containing 1 g of the exchanger in the H^+-form with a flow rate of ~0.5 ml min^{-1}. The effluent was titrated against a standard alkali solution of 0.1 M NaOH for the H^+ions eluted out. A maximum elution was observed with the concentration of 1 M $NaNO_3$ as indicated in Fig. 1.

2.6. Elution behavior

Since with optimum concentration for a complete elution was observed to be 1 M for sample T-1 (Fig. 2), a column containing 1 g of the cation-exchanger in H^+-form was eluted with $NaNO_3$solution of this concentration in different 10 ml fractions with minimum flow rate as described above. Each fractions of 10 ml effluent was titrated against a standard alkali solution for the H^+ ions eluted out (Fig. 2).

2.7. pH-titration

pH-titration studies of polypyrrole Th(IV) phosphate (T-1) was performed by the method of

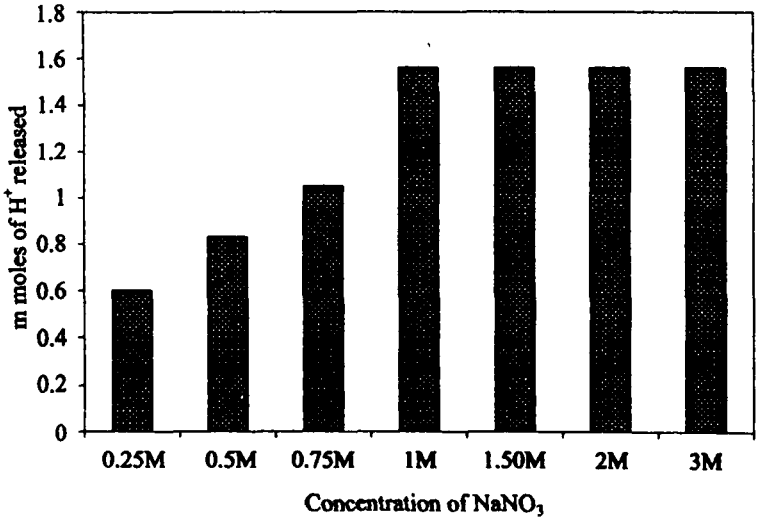

Fig. 1. Effect of eluent concentration on ion-exchange capacity of polypyrrole Th(IV) phosphate cation-exchanger.

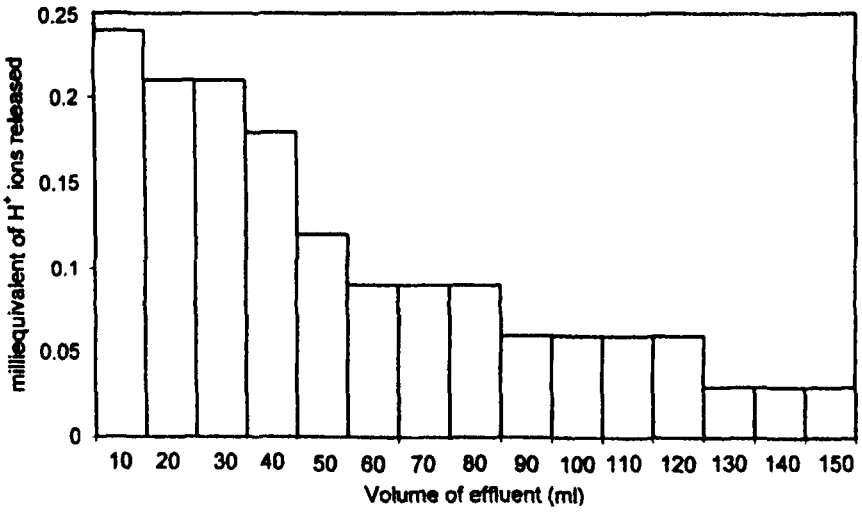

Fig. 2. Elution behavior of polypyrrole Th(IV) phosphate cation-exchange material.

Topp and Pepper [34]. A total of 500 mg portions of the cation-exchanger in the H^+-form were placed in each of the several 250 ml conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratio, the final volume being 50 ml to maintain the ionic strength constant. The pH of the solution was recorded every 24 h until equilibrium was attained which needed ~5 days and pH at equilibrium was plotted against the milliequivalents of OH^- ions added. The results are shown in Fig. 3.

2.8. Distribution (sorption) studies

The distribution coefficient (K_d values) of various metal ions on polypyrrole Th(IV) phosphate were determined by batch method in various solvents systems. Various 200 mg of the composite cation-exchanger beads (T-1) in the H^+-form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion concentration was to adjust that it did not exceed 3% of its total ion-exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solution of EDTA [35]. The alkali metal ions [K^+, Na^+, Ca^{2+}] were determined by flame photometry and some heavy metal ions such as [Pb^{2+}, Hg^{2+}, Zn^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution coefficient (K_d) values calculated using the formula given below:

$$K_d = \frac{\text{m moles of metal ions/gm of ion-exchanger}}{\text{m moles of metal ions/ml of solution}} \ (\text{ml g}^{-1}),$$

i.e.

$$K_d = (I - F)/F \times V/M \ (\text{ml g}^{-1}),$$

where I is the initial amount of the metal ion in the solution phase, F is final amount of metal ion in the solution phase. V is the volume of the solution (ml) and M is the amount of exchanger (g).

2.9. Separation factors

$$\text{Separation factor } (\alpha_B^A) = \frac{K_d(A)}{K_d(B)},$$

where K_d(A) and K_d(B) are the distribution coefficients for the two competing species A and B in the ion-exchange system.

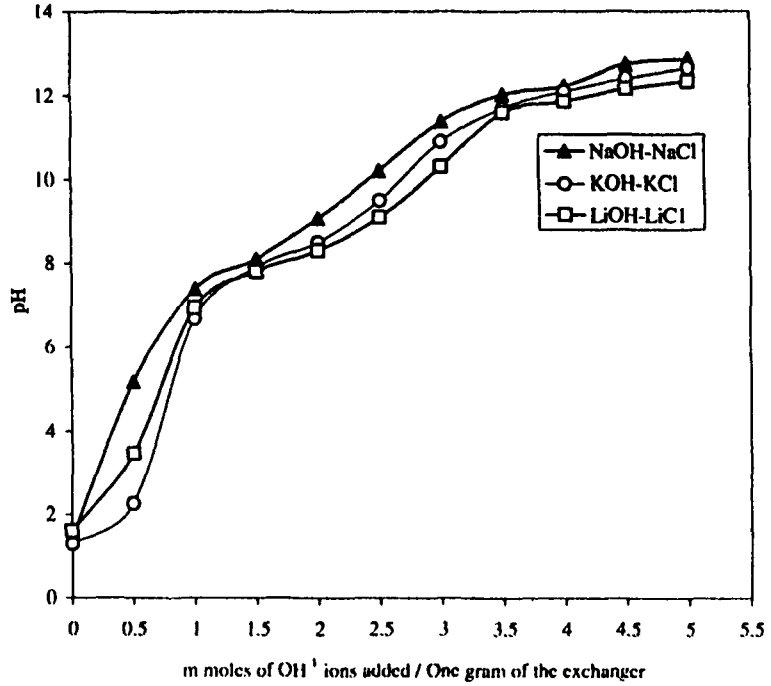

Fig. 3. pH-titration curves for polypyrrole Th(IV) phosphate composite cation-exchanger with various alkali metal hydroxides.

2.10. Quantitative separation of metal ions

Quantitative binary separations of some important metal ions of analytical utility were achieved on polypyrrole Th(IV) phosphate column. 1 g of the cation-exchanger (~125 μm) in H^+-form were used for column separations in a glass tube having an internal diameter of ~0.6 cm and a height of 35 cm. The column was washed thoroughly with DMW and the mixture of two metal ions having initial concentrations of 0.01 M each, to be separated was loaded on it and allowed for one hour to absorb the metal ions on the exchanger and then pass on to the column gently (maintaining a flow rate of 2–3 drops per minute) till the level was just above the surface of the material. After recycling two or three times to ensure complete absorption of the mixture on column beads, the separation was achieved by passing a suitable solvent at a flow rate of 1 ml min^{-1} through the column as eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration.

2.11. Preparation of polypyrrole Th(IV) phosphate membrane

The ion-exchange membrane was prepared by following the procedure of Coetzee and Benson [36]. Polypyrrole Th(IV) phosphate cation-exchanger (100 mg) as electroactive material was ground to fine powder, and was mixed thoroughly with Araldite (Ciba-Geigy, India Ltd.) (100 mg) in 1:1 (w/w) ratio to make a homogeneous paste, which was, then spread between the folds of Whatman's filter paper No. 42. Glass plates were kept below and above the filter paper folds as support. The phase of the exchanger and Araldite was kept under pressure of 2 kg cm^2 for 24 h and left to dry. Three sheets of different thickness 0.42, 0.50, 0.55 mm of master membranes was prepared. These sheets were dipped in distilled water to remove filter paper. After drying, the membrane sheets were cut in the shapes of discs using a sharp edge blade. The pre-requisite for understanding the performance of an ion-exchange membrane is its complete

physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters are membrane water content, porosity, thickness, swelling etc. and were determined as described elsewhere [37–39].

The conditional membranes were first soaked in water to elute diffusible salt, blotted quickly with Whatman filter paper to remove surface moisture and immediately weighed. It was further dried to a constant weight in a vacuum over P_2O_5 for 24 h. The water content (% total wet weight) was calculated as

$$\%\ \text{Total Wet Weight} = \frac{W_w - W_d}{W_w} \times 100,$$

where W_w = weight of the soaked/wet membrane and W_d = weight of the dry membrane.

Swelling is measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane.

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data:

$$\varepsilon = \frac{W_w - W_d}{AL\rho_w},$$

where W_w = weight of the soaked/wet membrane, W_d = weight of the dry membrane, A = area of the membrane, L = thickness of the membrane and ρ_w = density of water.

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauge.

2.12. Fabrication of ion-selective electrode

The membrane sheet of 0.42 mm thickness as obtained by the above procedure was cut in the shape of disc and mounted at the lower end of a pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) with Araldite. Finally the assembly was allowed to dry in air for 24 h. The glass tube was filled with solution of the ion (as internal reference) towards which the membrane is selective and kept dipped in an identical solution of the same ion at room temperature. In case of polypyrrole Th(IV) phosphate ion-selective membrane electrode, the glass tube was filled with 0.1 M lead nitrate solution. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as external reference electrode. The whole arrangement can be shown as

Internal reference electrode (SCE)	Internal electrolyte 0.1 M Pb^{2+}	Membrane	Sample solution	External reference electrode (SCE)

In advance of measurements of the electrode potential (at 25 ± 2 °C) for a series of standard solutions of $Pb(NO_3)_2$ (10^{-9}–10^{-1} M), the membrane of the electrode was conditioned by soaking in 0.1 M $Pb(NO_3)_2$ solution for 5–7 days and for 1 h at least before use. The experiments were conducted in air thermostat maintained at 25 ± 1 °C, when not in use the membrane electrode was removed from the test-solution and kept in a 0.1 M selective metal ion solution.

Potential measurements of the membrane electrode were plotted against the selected concentrations of the respective ions in aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system. In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time and working pH range.

The response time is measured by recording the e.m.f. of the electrode as a function of time when it is immersed in the solution to be studied. The electrode is usually first dipped in a 1×10^{-3} M solution of the ion concerned and immediately shifted to another solution (pH ≈ 4.0) of 1×10^{-2} M ion concentration of the same ion (10-fold higher concentration). The potential of the solution was read at zero second, i.e. just after immediate dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 s. The potentials were then plotted against the time. The time during which the potentials attain constant value represents the response time of the electrode.

A series of solutions of varying pH in the range of 1–13 were prepared, keeping the concentration of the relevant ion constant (1×10^{-3} M). The pH variations were brought about the addition of dilute acid (HCl) or dilute alkali (NaOH) solutions. The value of the electrode potential at each pH was recorded and plot of electrode potential versus pH was plotted.

To study the cationic interference due to other ions, the selectivity coefficients of various interfering cations for the ion-selective membrane electrode was determined by the mixed solution method as discussed elsewhere [40]. A beaker of constant volume contains a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-3} M) and varying concentrations (1×10^{-1} to 1×10^{-7} M) of the primary ion. Now the potential measurements were made using the membrane electrode assembly.

3. Result and discussion

In this paper, a novel sample of 'organic inorganic' composite cation-exchange material (sample T-1) was developed by incorporation of electrically conducting polymer, polypyrrole into the inorganic matrices of fibrous Th(IV) phosphate [31] by simultaneous gelation of inorganic acid salt as well as polymerization of pyrrole monomer using ferric chloride as oxidizing reagent. This material possessed a better Na^+ ion-exchange capacity, (1.56 meq g^{-1} as compared to the Th(IV) phosphate 0.72 meq g^{-1}). It was also found that the values of H^+-adsorption and H^+-liberation capacities are in close agreement (Table 1). The effect of the size and charge of the exchanging ion on the ion-exchange capacity was also observed for this material. The ion-exchange capacity of the composite cation-exchanger for alkali ions and alkaline earth metal ions increase according to the decrease in the hydrated ionic radii [41–43] (Table 1).

It was observed that the material was resistant to 2 M HCl, 2 M HNO_3, and 0.5 M H_2SO_4. The chemical dissolution in DMW, alkaline media, $NaNO_3$, NH_3, DMSO, acetone and *n*-butyl alcohol was almost negligible [44]. On heating at different temperatures for an hour, the mass, physical appearance and ion-exchange capacity of the dried sample material (T-1) were changed as the temperature increased as shown in Table 2. However, the material was found to possess higher thermal stability up to 150 °C and it remains about 56% of the initial ion-exchange capacity by heating up to 350 °C.

The column elution experiment indicated a dependence of the concentration of the eluent on the rate of elution, which is usual behavior, for such materials. The minimum molar concentration of $NaNO_3$ as eluent for sample T-1 was 1 M for maximum release of H^+ ions from 1 g of the cation-exchanger as evident from Fig. 1. The elution behavior indicates that the exchange is quite fast at the beginning as all the exchangeable H^+ ions are eluted out in the first 150 ml of the effluent (Fig. 2) from a column of 1 g exchanger within 5 h.

The pH-titration curves for polypyrrole Th(IV) phosphate (sample T-1) was obtained under equilibrium conditions with NaOH/NaCl, KOH/KCl and LiOH/LiCl, systems indicated bifunctional behavior of the materials as shown in Fig. 3. The composite material appear to be strong cation-exchanger as indicated by a low pH (~1.5) of the solutions when no OH^- ions were added to the system. For the sample T-1, the rate of H^+–Na^+ exchange was faster than those of H^+–K^+ and H^+ Li^+ exchanges. The adsorption behavior for alkali metals on this material was observed to be in the order of Na(I) > Li(I) > K(I) in acidic pH and Na(I) > K(I) > Li(I) in the basic media. The theoretical I.E.C. of T-1 for these ions were found to be ~2.5 meq g^{-1}.

On the basis of chemical composition studies and instrumental analyses (such as FTIR, TGA–DTA), the molar ratio of the elements in the proposed composite cation-exchange material was estimated to be Th:P:C:H:N:O:1:2.34:11.77:25.36:2.73:15.21 which can suggest the following formula of the material: $[(ThO_2)(H_3PO_4)_2 \cdot (-C_4H_2NH-)_3] \cdot nH_2O$ [44].

In order to explore the potentiality of this composite material (T-1) in the separation of metal ions, distribution studies for 17 metal ions were performed in 10 solvent systems. It is apparent from the data given in Table 3 that the K_d-

Table 3
K_d values of some metal ions on polypyrrole Th(IV) phosphate (T-1) in different solvent systems

Metal ions	DMW	1×10^{-3} M $HClO_4$	1×10^{-2} M $HClO_4$	1×10^{-1} M $HClO_4$	1×10^{-2} M HNO_3	1×10^{-1} M HNO_3	1 M HNO_3	1×10^{-2} M HCl	1×10^{-1} M HCl	1 M HCl
Na^+	18	17	12	7	10	7	5	12	7	3
K^+	114	80	37	14	31	18	12	41	16	13
Mg^{2+}	20	14	12	-	27	11	9	25	18	11
Ca^{2+}	106	80	18	11	13	8	3	73	22	-
Sr^{2+}	170	180	53	13	767	50	21	23	17	-
Ba^{2+}	650	367	150	114	88	50	36	180	133	56
Pb^{2+}	900	2000	900	233	1900	300	44	600	90	50
Zn^{2+}	63	40	13	4	19	11	5	21	-	-
Hg^{2+}	1100	800	767	333	830	600	-	314	67	29
Al^{3+}	20	40	133	100	120	25	-	120	400	-
Fe^{3+}	90	88	67	50	169	110	-	140	130	-
La^{3+}	87	81	65	61	70	61	-	47	35	-
Ce^{4+}	250	200	75	25	40	17	-	50	22	-
Zr^{4+}	700	600	400	350	800	750	-	1000	900	-
UO_2^{2+}	833	400	350	233	100	67	20	400	300	150
Tl^+	200	500	200	38	71	33	22	50	22	-
Ag^+	113	53	33	12	33	21	7	43	29	11

Table 4
Separation factors of different metal ions on polypyrrole Th(IV) phosphate

Separation factor	DMW	1×10^{-3} $HClO_4$	1×10^{-2} M HNO_3
α^{Pb}_{Zn}	14.3	50.0	100.0
α^{Pb}_{Mg}	45.0	142.9	70.4
α^{Pb}_{Al}	45.0	50.0	15.8
α^{Hg}_{Zn}	17.5	20.0	43.7
α^{Hg}_{Fe}	12.2	9.1	4.9

values can vary with the composition and nature of the contacting solvents. It was observed from the (K_d) values in DMW, 1×10^{-3} M $HClO_4$ and 1×10^{-2} M HNO_3 that Pb^{2+} and Hg^{2+} is strongly adsorbed; Ba^{2+}, Zr^{4+}, UO_2^{2+}, Ce^{4+}, Tl^+ are also significantly adsorbed while the remaining are partially adsorbed. The high uptake of certain metal ions demonstrates not only the ion-exchange properties but also the adsorption and ion-sieve characteristics of the cation-exchanger material.

On the basis of K_d values, separation factor for some metal ion pairs were calculated and given in Table 4. The most promising property of these materials was found to be the high selectivity towards Pb(II), indicating its importance in environmental studies. The separation capability of the material has been demonstrated by achieving some important binary separations of different synthetic

Table 5
Some binary separation of metal ions achieved on polypyrrole Th(IV) phosphate

Separation achieved	Amount loaded (μg)	Amount found (μg)	% error	Eluent used	Volume of eluent (ml)
Zn(II)	1307.4	1294.3	−1.00	0.01 M HNO_3	50
Pb(II)	4144.0	4144.0	0.00	0.1 M $HClO_4$	60
Mg(II)	729.2	731.6	+0.33	DMW	60
Pb(II)	3108.2	3087.3	−0.67	0.1 M $HClO_4$	50
Al(III)	809.4	808.1	−0.16	0.01 M $HClO_4$	60
Pb(II)	3108.4	3159.8	+1.65	0.1 M $HClO_4$	50
Zn(II)	1307.4	1307.4	0.00	0.01 M HNO_3	50
Hg(II)	3510.3	3560.5	+1.43	0.1 M HCl	60
Fe(III)	1117.0	1111.5	−0.49	0.01 M $HClO_4$	50
Hg(II)	3008.9	3028.9	+0.66	0.1 M HCl	50

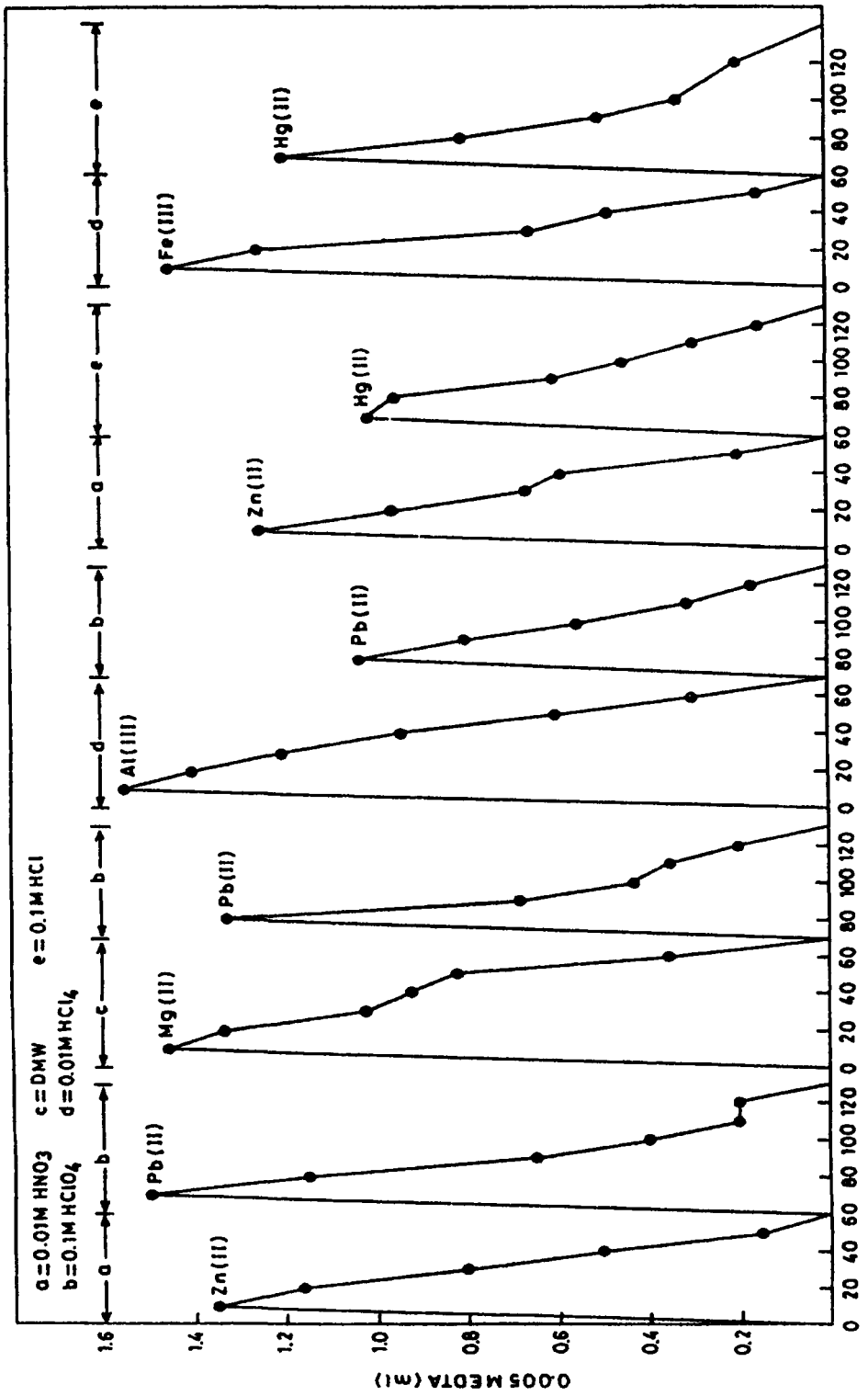

Fig. 4. Binary separations of Pb(II) from Zn(II), Mg(II), Al(III), and Hg(II) from Zn(II), Fe(III), on polypyrrole Th(IV) phosphate column.

Table 6
Characterization of ion-exchanger membrane

Polypyrrole Th(IV) phosphate membranes	Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
M-1	0.42	4.88	0.064	0.2
M-2	0.50	5.61	0.094	0.2
M-3	0.55	7.87	0.112	0.2

metal mixtures involving Pb(II), for example: Pb^{2+}–Zn^{2+}, Pb^{2+}–Mg^{2+} and Pb^{2+}–Al^{3+}.

Table 5 summarizes the salient features of these separations. The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). It was also observed that Pb (II) retained strongly on the cation-exchanger column. The weakly retained metal ions appear out of the column faster than Pb (II) and Pb (II) was eluted after by $HClO_4$ solution. The order of elution and eluents used for some representative binary separations are also illustrated in Fig. 4.

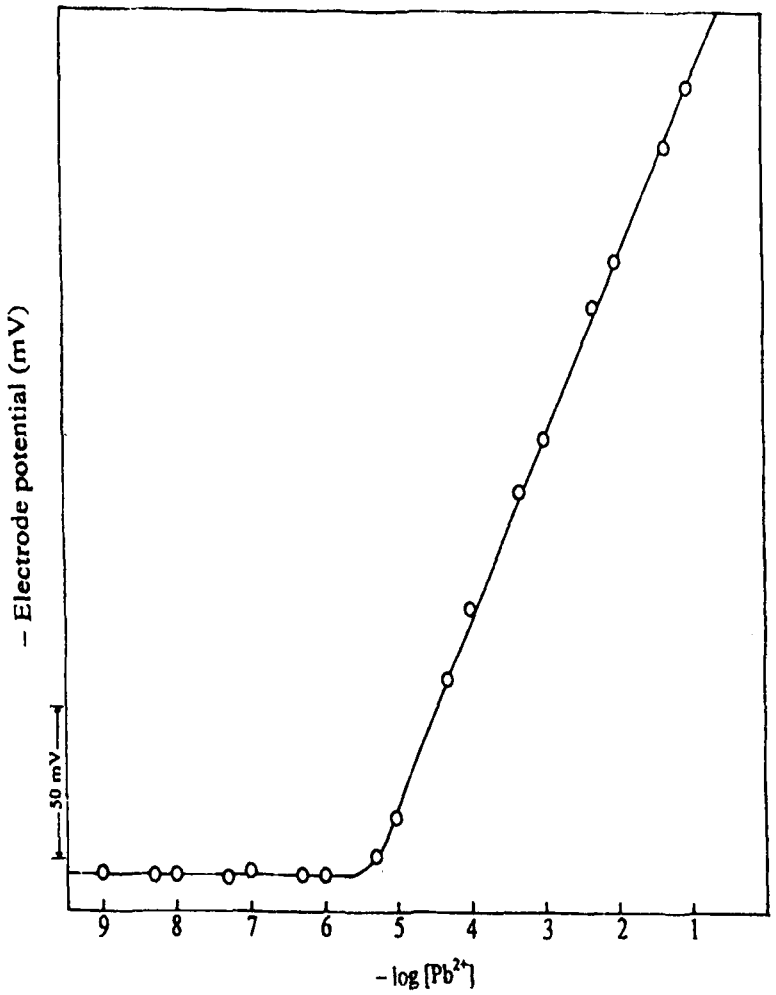

Fig. 5. Calibration curve for polypyrrole Th(IV) phosphate membrane electrode in aqueous solution of $Pb(NO_3)_2$.

The separations are quite sharp and recovery is quantitative and reproducible. It was also observed from the distribution studies that the cation-exchanger was also found to be selective for Hg(II). Some binary separations (Hg^{2+}-Zn^{2+}, Hg^{2+}-Fe^{3+}) involving Hg(II) was also carried out on the proposed composite cation-exchanger column (Table 5).

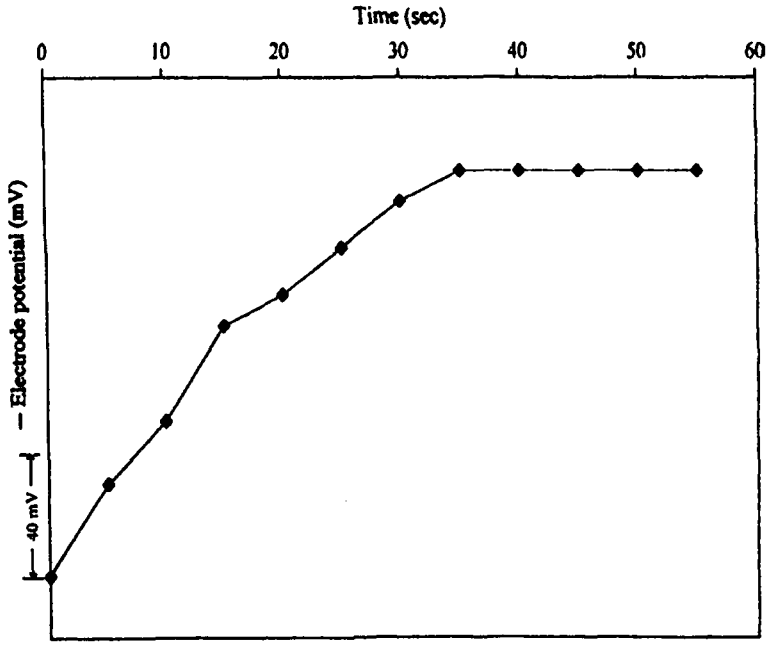

Fig. 6. Response of Pb^{2+} ion-selective polypyrrole Th(IV) phosphate membrane electrode at different time interval.

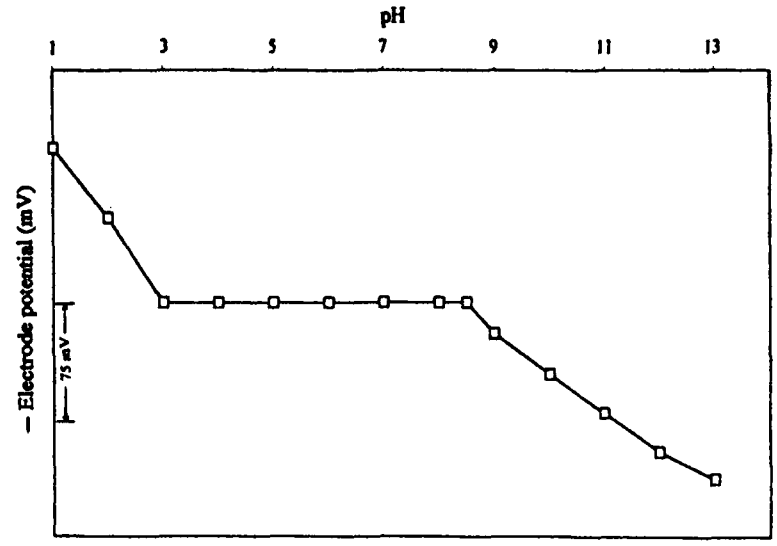

Fig. 7. Effect of pH on electrode response of Pb^{2+} ion-selective polypyrrole Th(IV) phosphate membrane electrode.

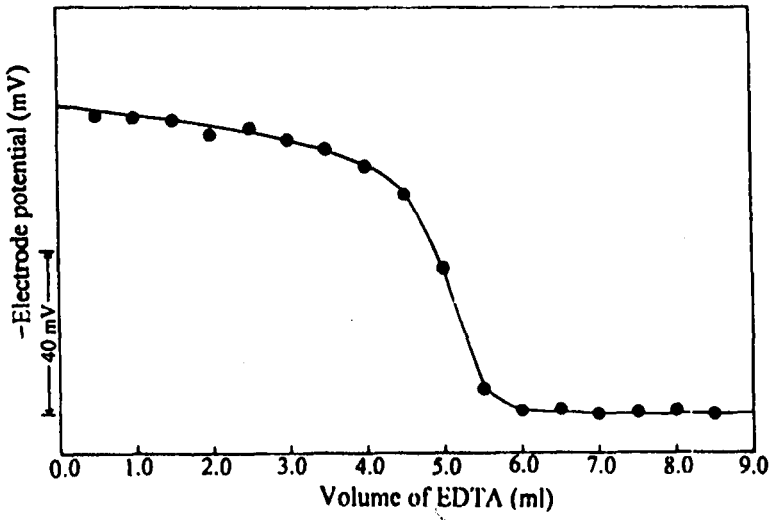

Fig. 8. Precipitation titration of Pb(II) against EDTA solution.

A number of samples for the polypyrrole Th(IV) phosphate membranes were prepared with different amounts of Araldite and checked for the mechanical stability, surface uniformity, material distribution, cracks and thickness etc. But the membranes obtained with 50% Araldite (w/w) were found to be good, and show the best mechanical stability as well as electro-chemical performance.

The thickness, swelling, porosity, water content capacity etc. of the polypyrrole Th(IV) phosphate cation-exchanger membrane was investigated and the results are summarized in Table 6. The swelling should also be small for a membrane to exhibit good electrochemical performance. The membrane sample M-1 (thickness 0.42 mm) was selected for further studies. Thus, the low order of water content, swelling and porosity with less thickness of this membrane suggest that interstices are negligible and diffusion across the membrane would occur mainly through the exchange sites.

The heterogeneous precipitate Pb(II) ion-selective membrane electrode obtained from polypyrrole Th(IV) phosphate cation-exchanger material gives linear response (Fig. 5) in the given range of 1×10^{-1} to 5×10^{-6} molar with a slope of 29.17 mV per decade change in Pb(II) ion concentration, the slope value is close to Nerstian value, 29.6 mV per concentration decade for divalent cations. A constant potential was obtained after 35 seconds (Fig. 6) and it was also observed that electrode potential remained unchanged with in the pH range of 3.0 8.5 (Fig. 7). The selectivity coefficients, $K^{POT}_{Pb.M}$ of various differing cation for the Pb(II) ion-selective polypyrrole Th(IV) phosphate membrane electrode were determined, by the mixed solution method [40] and the following values are obtained:

Membrane electrode	Selectivity coefficients ($K^{POT}_{Pb.M}$) for interfering cations (M^{n+})										
	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Hg^{2+}	Al^{3+}	Fe^{3+}
Polypyrrole thorium(IV) phosphate	0.016	0.018	0.024	0.012	0.080	0.023	0.011	0.026	0.032	0.052	0.040

The results reveal that the electrode is selective for Pb(II) in presence of interfering cations.

The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometric titration of 0.01 M $Pb(NO_3)_2$ solution against EDTA solution as a titrant (Fig. 8). For this, 5 ml $Pb(NO_3)_2$ solution was pipeted out in a beaker, its volume was raised up to 20 ml by DMW. This solution was titrated against EDTA solution; electrode potential was measured after each addition of 0.5 ml. The necessary adjustment of pH (≈4) was made before adding the titrant. The addition of EDTA causes a decrease in potential as a result of the decrease in free Pb(II) ion concentration due to its complexation with EDTA. The amount of Pb(II) ions in solutions can be accurately determined from the resulting neat titration curve providing a sharp end point. The potentiometric titration of Pb(II) was also successfully carried out in the presence of 1×10^{-5} M Ni(II), Cu(II) and Zn(II), hence demonstrating the usefulness of the sensor developed for potentiometric determination of Pb(II) in mixtures.

4. Conclusions

A fibrous type organic–inorganic hybrid material polypyrrole Th(IV) phosphate was prepared by the incorporation of electrically conducting polymer, polypyrrole into the inorganic precipitate of Th(IV) phosphate behaves as a cation-exchange material. It possessed better ion-exchange capacity and is highly selective for Pb(II). This adsorption behavior of this cation-exchanger is promising in the field of environmental chemistry where an effective detection and separation method is needed for Pb(II) from other pollutants. It is evident from the results that the quantitative and efficient separations of various metal ions, such as Pb(II) from Zn(II), Mg(II), Al(III) and Hg(II) from Zn(II), Fe(III) etc., are feasible on polypyrrole Th(IV) phosphate column. Using this electroactive material, chemically and mechanically stable Pb(II) ion-sensitive membrane electrode was also developed that gives reproducible results with a useful lifetime, exhibiting a nearly Nernstian slope (29.17 mV per concentration decade) within functional pH range of 3.0–8.5. Further, the electrode can be used to determine Pb(II) ions in aqueous media by both direct potentiometry and titration, and can successfully be used in determining Pb(II) ions in real samples.

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Applications of Hg(II) sensitive polyaniline Sn(IV) phosphate composite cation-exchange material in determination of Hg^{2+} from aqueous solutions and in making ion-selective membrane electrode

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Abstract

Polyaniline Sn(IV) phosphate an 'organic–inorganic' composite material, was prepared via sol–gel mixing of organic polymer polyaniline into the matrices of the inorganic precipitate of Sn(IV) phosphate. The ion-exchange capacity and distribution coefficients with respect to various metal ions were determined on the column of polyaniline Sn(IV) phosphate. The distribution studies showed the selectivity of Hg(II) ions by this material. However, the sensitivity level of Hg(II) ions on the composite material was determined quantitatively. Hg(II) ions were separated and determined from the binary aqueous mixtures of Hg(II)–Cu(II), Hg(II)–Ni(II), Hg(II)–Cd(II), Hg(II)–Co(II), Hg(II)–Al(III), etc. For the determination of Hg(II) ions in aqueous solutions, a Hg(II) ion sensitive membrane electrode was prepared by means of this composite cation-exchanger as the electroactive material. The membrane electrode was mechanically stable with quick response time and could be operated over a wide pH range with a slope of 30 mV per decade change in a linear concentration range of 1×10^{-1} to 1×10^{-6} M. The selectivity coefficients were determined by the mixed solution method and revealed that the electrode was selective for Hg(II) in the presence of interfering cations. The practical utility of this electrode was established by employing it as an indicator electrode in the potentiometric titration of Hg(II).

Keywords: Composite cation-exchanger; Determination of Hg(II); Polyaniline Sn(IV) phosphate; Hg(II) ion-selective membrane electrode

1. Introduction

Over the past decades ion-selective electrode based potentiometry has become a well-established electroanalytical technique. In this technique the most exciting and fastest growing area of research is the use of ion sensitive membrane electrodes for analysis of wastewater containing heavy metals. Using this approach the applicability of the potentiometric method has been greatly extended enabling the simple and accurate determinations of many heavy metal ions and has led to a search for suitable materials that can be used for preparation of sensitive and selective ion-sensors, chemical sensors or more commonly ion-selective electrodes (ISEs). Precipitate based ion-selective membrane electrodes are well known as they are successfully employed for the determination of several anions and cations [1–12]. There are some homogeneous as well as heterogeneous hybrid ion-exchange membranes. Homogeneous ion-exchange membranes are coherent ion-exchanger gels in the shape of disks, ribbons, etc. The heterogeneous precipitate ion-exchange membranes consisting of suitable colloidal ion-exchanger particles as electroactive materials embedded in a polymer (inert) binder, i.e., poly(vinyl chloride) (PVC), or epoxy resin (Araldite), or polystyrene, polyethylene, nylon, PMMA, etc., have been extensively studied as potentiometric sensors [13–24]. The use of 'organic–inorganic' composite ion-exchange materials formed by the combination of inorganic precipitates and organic polymers as electroactive components in membrane electrodes has generated widespread interest in developing new ion-selective electrodes (ISEs) for sensor applications [25], especially for the determination of heavy toxic metals [26–28].

Mercury is a toxic persistent bioaccumulative pollutant that affects the nervous system. It is found as industrial waste

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because of its growing area in production of some batteries, thermometers, cameras, cathode tubes, calculators, medical laboratory chemicals, a catalyst in production of urethane polymers for plastics, a cathode in electronic production of chlorine and caustic soda, mercury vapor lamps and barometers. Methyl mercury is a chemical species that bioaccumulate in fish. Fish consumption advisories are in effects for mercury in thousands of lakes and rivers, including much of the Great lakes ecosystem.

The harmful effects of mercury may cause cancer, damages of the stomach, large intestine and lungs, and can also increase blood pressure and heart rate. Thus, it is very important to determine mercury at lower and lower levels in our environments. Although various common methods are used to determine mercury such as complexometry [29], spectrophotometry, flame and atomic absorption spectrometry, inductively coupled plasma, fluorimetry, X-ray fluorescence, voltametery and potentiometry [30]. Recently, composite materials are well known and used for the fabrication of various electrometric sensors for analytical purposes [31–35]. In our present research work, a Hg(II) sensitive polyaniline Sn(IV) phosphate composite cation-exchange material is prepared and used in making an ion-selective membrane electrode for various analytical studies.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, GSC, E-merck (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), a double beam atomic absorption spectrophotometer (GBC 902, Australia), a digital flame photometer (Elico CL 22D, India), a UV/vis spectrophotometer (Elico EI 301E, India), a water bath incubator shaker, a digital potentiometer (Equiptronics EQ 609, India) with a saturated calomel electrode as a reference electrode were used.

2.2. Preparation of polyaniline Sn(IV) phosphate organic–inorganic composite cation-exchanger

The 'organic–inorganic' composite cation-exchanger polyaniline Sn(IV) phosphate was prepared as reported earlier [36]. The organic polymer polyaniline was prepared by mixing different volumes of the solution of 10% aniline ($C_6H_5NH_2$) and 0.1 M potassium persulphate ($K_2S_2O_8$) prepared in 1 M HCl with continuous stirring by a magnetic stirrer for half an hour at 0 °C, and green colored gels were obtained. These gels were transferred into the white precipitates of Sn(IV) phosphate prepared at room temperature (25 ± 2 °C) and at pH 1 by adding different (V/V) ratios of 0.1 M stannic chloride solution to an aqueous solution of 0.1 M di-sodium hydrogen orthophosphate (Na_2HPO_4). The resultant green colored gels were kept for 24 h at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was decanted and the gels were filtered by suction. The excess acid was removed by washing with demineralized water (DMW) and the material was dried in an air oven at 50 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H^+-forms by treating with 1 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and finally dried at 50 °C. The particles size of ~125 μm of the material was obtained by sieving and kept in desiccators. Hence, different samples of the 'polyaniline Sn(IV) phosphate' composite cation-exchanger were prepared and on the basis of the Na^+ ion-exchange capacity determined by column process, the percentage of yield and physical appearance of beads sample S-1 was selected for further studies. The results are given in Table 1.

2.3. Distribution (sorption) studies

The distribution coefficients (K_d values) of various metal ions on polyaniline Sn(IV) phosphate were determined by a batch method in various solvent systems. Various 200 mg of the composite cation-exchanger beads (S-1) in the H^+-form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion concentration was adjusted so that it did not exceed 3% of its total ion-exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against a standard 0.005 M solution of EDTA [37]. The alkali metal ions [K^+, Na^+, Ca^{2+}] were determined by flame photometry and some heavy metal ions such as [Pb^{2+}, Hg^{2+}, Zn^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution coefficient (K_d) values were calculated by using the formula given below:

$$K_d = \frac{\text{mmoles of metal ions/g ion-exchanger}}{\text{mmoles of metal ions/ml solution}} (\text{ml g}^{-1}) \quad (1)$$

i.e., $K_d = [(I - F)/F] \times (V/M)$ (ml g^{-1}), where I is the initial amount of the metal ion in the solution phase, F is the final

Table 1
Conditions of preparation and the ion-exchange capacity of polyaniline Sn(IV) phosphate composite cation-exchange material

Sample	Mixing volume ratio					Appearance of beads after drying	Na^+ ion-exchange capacity (meq dry g^{-1})
	0.1 M $SnCl_4 \cdot 5H_2O$ in 4 M HCl	0.1 M Na_2HPO_4 in DMW	pH of the inorganic precipitate	0.1 M $K_2S_2O_8$ in 1 M HCl	10% Aniline in 1 M HCl		
S-1	2	3	1.0	1	1	Greenish granular	1.96
S-2	2	3	1.0	–	–	White granular	1.12

amount of the metal ion in the solution phase, V is the volume of the solution (ml) and M is the amount of the exchanger (g).

2.4. Separation factor

The separation factor may be considered as the relative tendency of two ions to be adsorbed in an exchanger from solutions of equal concentration. It is used as a measure of possibility of chromatographic separation and is also expressed as the ratio of the distribution coefficients of the elements to be separated as:

$$\text{Seperation factor}\,(\alpha_B^A) = \frac{K_d(A)}{K_d(B)} \quad (2)$$

where K_d (A) and K_d (B) are the distribution coefficients for the two competing species A and B in the ion-exchange system.

2.5. Quantitative separation of metal ions

Quantitative binary separations of some important metal ions of analytical utility were achieved on the polyaniline Sn(IV) phosphate column. One gram of the cation-exchanger (~125 μm) in the H^+-form was used for column separations in a glass tube having an internal diameter of ~0.6 cm and a height of 35 cm. The column was washed thoroughly with DMW. The mixture of two metal ions having an initial concentration of 0.01 M each was loaded on the column and allowed for 1 h to adsorb the metal ions on the exchanger. The mixture was then passed on to the column gently (maintaining a flow rate of 2–3 drops/min) till the level was just above the surface of the material. After recycling two or three times to ensure complete adsorption of the mixture on column beads, the separation was achieved by passing a suitable solvent at a flow rate of 1 ml min^{-1} through the column as the eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration.

2.6. Preparation of polyaniline Sn(IV) phosphate membrane

The method of preparation of the ion-exchange membrane of polyaniline Sn(IV) phosphate was very similar to that of Coetzee and Benson [16]. The electroactive material, i.e., polyaniline Sn(IV) phosphate cation-exchanger was grinded to fine powder, and was mixed thoroughly with PVC, dissolved in 10 ml of tetrahydrofuran (THF) and finally mixed with 10 drops of dioctylphthalate used as a plastisizer [38]. The mixing ratio of the ion-exchanger was varied with a fixed content of PVC in order to obtain a composition, which gave the membrane showing the best performance, and the resulting solutions were carefully poured into a glass-casting ring (diameter 10 mm) resting on a glass plate. These rings were left for slow evaporation of THF to obtain thin films. In this way four sheets of different thickness of master membranes were obtained.

2.7. Characterization of membrane

The pre-requisite performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters were membrane water content, porosity, thickness, swelling, etc. and were determined as described elsewhere [39–42] after conditioning the membrane as given below.

2.7.1. Conditioning of the membrane

The membranes were conditioned by equilibrating with 1 M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH 5–6.5 (to neutralize the acid present in the film).

2.7.2. Water content (% total wet weight)

The conditioned membranes were first soaked in water to elute diffusible salts, blotted quickly with Whatman filter paper to remove surface moisture, and immediately weighed. These were further dried to a constant weight in vacuum over P_2O_5 for 24 h. The water content (% total wet weight) was calculated as:

$$\%\,\text{Total wet weight} = \frac{W_w - W_d}{W_w} \times 100 \quad (3)$$

where W_w is the weight of the soaked/wet membrane and W_d is the weight of the dry membrane.

2.7.3. Porosity

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data:

$$\varepsilon = \frac{W_w - W_d}{AL\rho_w} \quad (4)$$

where A is the area of the membrane, L is the thickness of the membrane and ρ_w is the density of water.

Table 2
Characterization of ion-exchanger membrane

S. no.	Membrane composition			Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
	Polyaniline Sn(IV) phosphate (mg)	PVC (mg)	Plasticizer (drops)				
M-1	100	200	10	0.36	2.25	0.074	0.2
M-2	150	200	10	0.46	3.29	0.101	0.2
M-3	200	200	10	0.56	15.73	0.321	0.2
M-4	250	200	10	0.78	16.63	0.573	0.2

Table 3
K_d-values of some metal ions on polyaniline Sn(IV) phosphate column in different solvent systems

Metal ions	DMW	10^{-3} M HNO_3	10^{-2} M HNO_3	10^{-1} M HNO_3	10^{-3} M HCl	10^{-2} M HCl	10^{-1} M HCl	0.1 M CH_3COOH + 0.1 M CH_3COONa (1:2)	0.1 M CH_3COOH + 0.1 M CH_3COONa (2:1)	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)
Cu^{2+}	771	600	250	283	650	258	38	967	1900	140
Co^{2+}	400	525	700	700	562	377	420	367	900	150
Ni^{2+}	237	400	210	150	275	71	67	100	1150	–
Hg^{2+}	4300	3500	3500	2900	2200	2360	1180	2600	3700	900
Cd^{2+}	1169	1150	1125	691	311	128	120	375	1428	112
Mn^{2+}	217	160	150	67	133	110	55	145	340	115
UO_2^{2+}	1000	500	434	329	425	378	269	716	900	412
Al^{3+}	1200	900	820	540	700	230	160	250	472	120
La^{3+}	120	85	74	56	62	42	–	148	183	36
Ce^{4+}	1700	1400	1400	766	1000	966	88	1320	3000	72
Zr^{4+}	900	700	350	250	850	729	–	600	850	300

2.7.4. *Thickness and swelling*

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze.

Swelling was measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane. The results of the membrane characterization are given in Table 2.

2.8. *Fabrication of ion-selective electrode*

The membrane sheet (M-1) of 0.36 mm thickness as obtained by the above procedure was cut in the shape of disc and mounted at the lower end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) with Araldite. Finally the assembly was allowed to dry in air for 24 h. The glass tube was filled with a 0.1 M mercuric nitrate $Hg(NO_3)_2$ solution. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as:

Internal reference electrode (SCE)

|Internal electrolyte 0.1 M Hg^{2+}|Membrane|

Sample solution|External reference electrode (SCE)

The response of the electrode in terms of the electrode potential (at 25 ± 2 °C), corresponding to the concentration of a series of standard solutions of $Hg(NO_3)_2$ (10^{-9} to 10^{-1} M), was determined at a constant ionic strength as described by IUPAC Commission for Analytical Nomenclature [43]. The membrane electrode was conditioned by soaking in a 0.1 M $Hg(NO_3)_2$ solution for 5–7 days and for 1 h at least before use. The experiments were conducted in air thermostat maintained at 25 ± 1 °C. After performing, the experiment membrane electrode was removed from the test-solution and kept in a 0.1 M $Hg(NO_3)_2$ solution.

Potential measurements of the membrane electrode were plotted against the selected concentrations of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system. In order to study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time and working pH range.

The response time was measured by recording the e.m.f. of the electrode as a function of time when it was immersed in the solution to be studied. The electrode was usually first dipped in a 1×10^{-3} M solution of the ion concerned and immediately shifted to another solution (pH ≈ 4.0) of 1×10^{-2} M ion concentration of the same ion (10-fold higher concentration). The potential of the solution was read at zero second, that is, just after immediate dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 s. The potentials were then plotted against the time. The time during which the potentials attain a constant value represents the response time of the electrode.

A series of solutions of varying pH in the range of 1–14 were prepared, keeping the concentration of the relevant ion constant (1×10^{-3} M). The pH variations were brought about the addition of dilute acid (HCl) or dilute alkali (NaOH) solutions. The value of the electrode potential at each pH was recorded and was plotted against pH.

To study the cationic interference due to other ions, the selectivity coefficients of various interfering cations for the ion-selective membrane electrode was determined by the mixed solution method as discussed elsewhere [44]. A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) (1×10^{-3} M) and varying concentrations (1×10^{-1} to 1×10^{-9} M) of the primary ion. Now the potential measurements were made by using the membrane electrode assembly.

3. Results and discussions

Polyaniline Sn(IV) phosphate, an organic–inorganic composite cation-exchanger, was prepared by sol–gel mixing of an organic polymer, i.e., polyaniline into the white inorganic precipitate of Sn(IV) phosphate, and used as an electroactive material for the preparation of an ion-selective membrane electrode. This composite material possessed a better Na^+ ion-exchange capacity (1.96 meq dry g^{-1}) as compared to Sn(IV) phosphate

Table 4
Separation factors of different metal ions on polyaniline Sn(IV) phosphate

Separation factor	DMW	1×10^{-2} M HNO_3	1×10^{-1} M HNO_3	1×10^{-1} M HCl	0.1 M CH_3COOH + 0.1 M CH_3COONa (2:1)
α^{Hg}_{Cu}	5.57	14	10.25	31.05	2.69
α^{Hg}_{Ni}	18.14	16.67	19.33	17.61	26
α^{Hg}_{Cd}	3.68	3.11	4.20	9.83	6.93
α^{Hg}_{Co}	10.75	5.00	4.12	2.80	7.08
α^{Hg}_{Al}	3.58	4.27	5.37	7.38	10.4

(1.12 meq dry g^{-1}), as evident from Table 1. To find out the selective nature of this composite material (S-1) in the separation of metal ions as well as for the preparation of an ion-selective membrane electrode, distribution studies of 11 metal ions were achieved in different solvent systems. The results of distribution studies (Table 3) indicated that K_d values varied with the nature and composition of contacting solvents. It was also observed from the distribution studies (K_d values) that the Hg^{2+} was highly adsorbed in all solvents, while remaining metal ions were poorly adsorbed. The high uptake of mercury ions in all solvents demonstrate not only the ion-exchange properties but also the adsorption and ion-selective characteristics of the cation-exchanger. Thus, we can say that this composite cation-exchanger is highly selective for mercury and can be very well utilized for the determination and separation of mercury from waste effluents.

To demonstrate the separation capability of this composite cation-exchanger, separation factors of some metal ion pairs were also calculated and are given in Table 4. These separation factors clarify that the separations are feasible and can be achieved easily. Thus, on the basis of separation factors some important binary separations of different synthetic metal mixtures involving Hg(II) were accomplished on its column and the results are given in Table 5. The sequential elution of ions from the column depends upon the stability of metal-eluting ligand (eluent). It was also observed that Hg(II) retained strongly on the cation-exchanger column. The weakly retained metal ions came out of the column faster than Hg(II). Hg(II) was eluted after by a 0.1 M HNO_3 + 0.1 M NH_4NO_3 solution. The order of elution and eluents used for some representative binary separations are also illustrated in Fig. 1. The separations are quite sharp and recovery is quantitative and reproducible.

Four samples of polyaniline Sn(IV) phosphate based on PVC cation-selective membranes were prepared using different mixing ratios of electroactive polyaniline Sn(IV) phosphate and PVC dissolved in tetrahydrofuran (THF) with a fixed amount (10 drops) of plastisizer dioctylphthalate. The amount of the ion-exchanger was varied to change the thickness of the membranes coating. These membranes were characterized to find out one membrane of good electrochemical performance for the purpose of preparation of an ion-selective membrane electrode and the results are given in Table 2. It is observed that as the amount of electroactive polyaniline Sn(IV) phosphate increased, the thickness, swelling, water content, porosity increased. Thus, the low orders of water content, swelling and porosity with less thickness of this membrane suggest that interstices are negligible and diffusion across the membrane would occur mainly through the exchange sites. Hence, membrane sample M-1 (thickness 0.36 mm) was selected for the preparation of the ion-selective electrode for further studies.

The heterogeneous precipitate based membrane electrode, prepared from membrane sample M-1, showed a linear Nernstian response, as shown in Fig. 2, for the Hg(II) ions in the concentration range of 1×10^{-1} to 1×10^{-6} M at a fixed ionic strength by adding a suitable excess of electrolyte with an average slope of 30 mV/decade change in concentration. Thus, the working concentration range was found to be 1×10^{-1} to 1×10^{-6} M for Hg^{2+} ions.

A calibration curve was made by measuring the electrode response to standard solutions prepared by serial dilution with-

Table 5
Some binary separation of metal ions achieved on polyaniline Sn(IV) phosphate composite cation-exchanger

Separation achieved	Amount loaded (μg)	Amount found (μg)	Difference (%)	Eluent used	Volume of eluent (ml)
Cu(II)	953.10	949.92	−0.33	0.01 M HCl	50
Hg(II)	2005.90	1995.87	−0.50	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Ni(II)	1467.75	1467.75	0.00	0.01 M HCl	60
Hg(II)	3008.85	2998.82	−0.33	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Cd(II)	2248.00	2242.38	−0.25	0.1 M HCl	50
Hg(II)	3510.33	3490.27	−0.57	0.1 MHNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Co(II)	883.95	875.11	−1.00	0.01 M HCl	50
Hg(II)	3008.85	3008.85	0.00	0.1 MHNO_3 + 0.1 M NH_4NO_3 (1:1)	50
Al(III)	741.95	741.95	0.00	0.01 M HCl	60
Hg(II)	2005.90	2005.90	0.00	0.1 MHNO_3 + 0.1 M NH_4NO_3 (1:1)	50

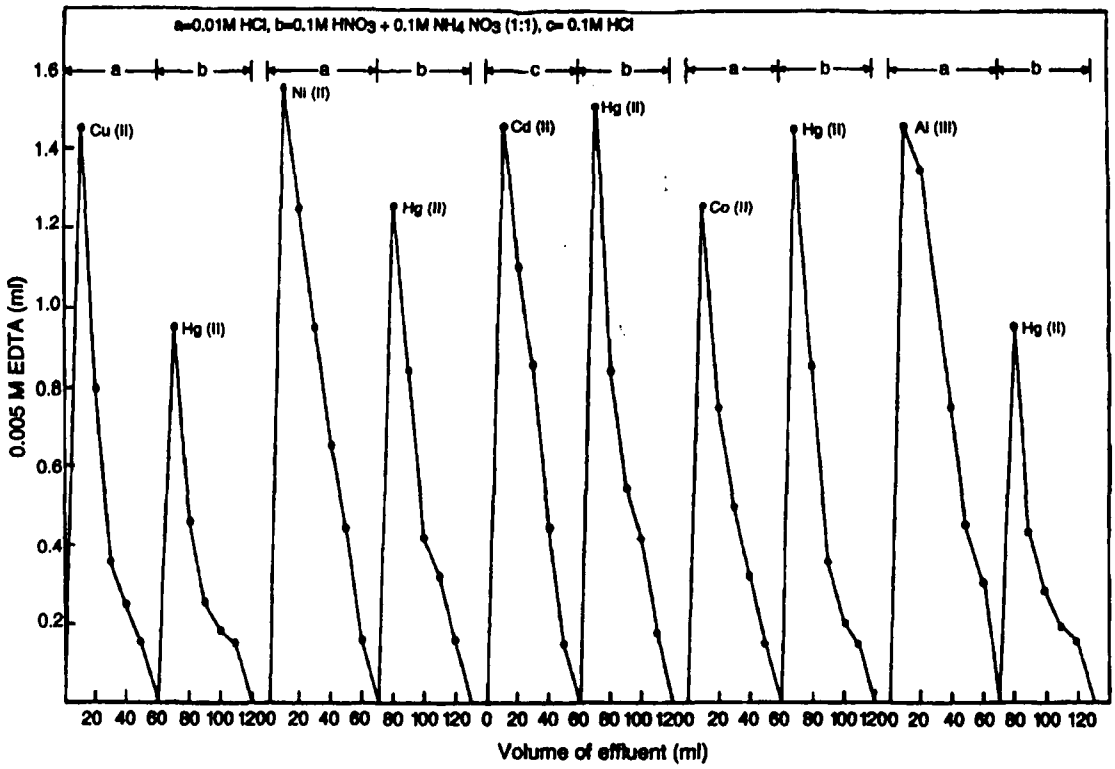

Fig. 1. Binary separations of Hg(II) from Cu(II), Ni(II), Cd(II), Co(II) and Al(III) on the polyaniline Sn(IV) phosphate column.

out the addition of extra indifferent salts. The ionic strength will increase linearly with an increase in concentration. This will lead to a gradual decrease of the activity coefficient, and the calibration curve [E versus log(concentration)] showed a negative deviation from the straight line for concentrations above 10^{-3} to 10^{-2} M. This curvature of the calibration curve can be precluded by working at a constant ionic strength. This is commonly achieved by adding a large excess of an indifferent electrolyte, the ionic strength buffer.

The response time of the stabilized electrode potential of the polyaniline Sn(IV) phosphate membrane electrode (±2 mV) was found 40 s, as is evident from Fig. 3. Although the solid contact electrodes are often criticized for their poor response and stability, the response of this electrode is quick and the lifetime is reasonable, at least 3 months. It is very important that the performance of any ion-selective electrode should be checked sooner every time before using it for any analytical purpose. For the present polyaniline Sn(IV) phosphate membrane electrode, it was observed that the measured potential of Hg^{2+} ions in a given concentration range of 10^{-1} to 10^{-9} M was reproducible within ±3 mV and there was no significant change in the slope

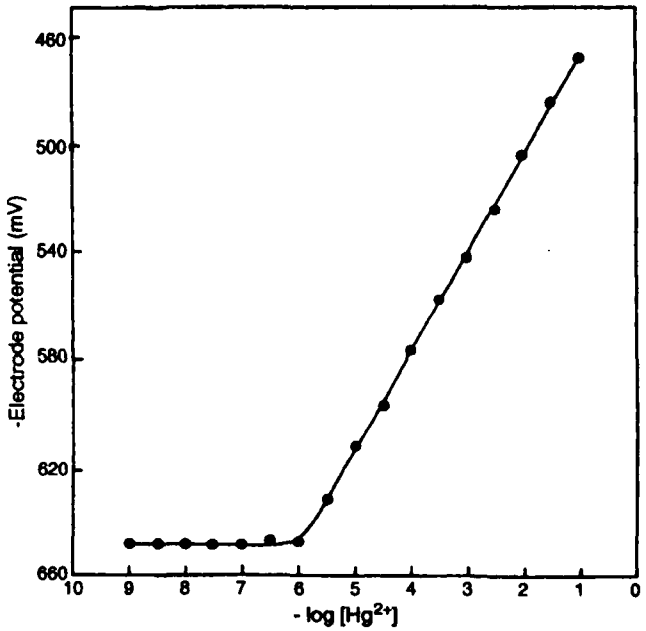

Fig. 2. Calibration curve for polyaniline Sn(IV) phosphate membrane electrode in aqueous solution of $Hg(NO_3)_2$.

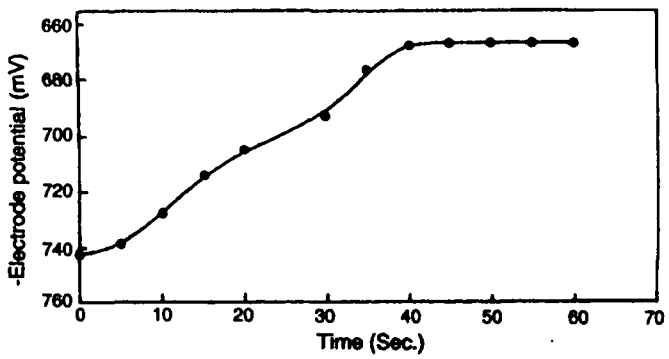

Fig. 3. Response of Hg^{2+} ion-selective polyaniline Sn(IV) phosphate membrane electrode at different time interval.

Table 6
Comparison of the response characteristics of different Hg^{2+} ion-selective electrodes

S. no.	Working concentration range (M)	Life time	pH range	Response time	Slope (mV)/decade	Reference
1	1×10^{-1} to 1×10^{-5}	Not mentioned	Not mentioned	Not mentioned	58.0	[45]
2	1×10^{-1} to 1×10^{-4}	Not mentioned	2.0–12.8	Not mentioned	27.0	[46]
3	1×10^{-1} to 1×10^{-5}	5 weeks	1.0	4 min	Not mentioned	[47]
4	1×10^{-1} to 1×10^{-5}	5 weeks	0–2.0	Less than 3 min	28.5	[48]
5	1×10^{-1} to 1×10^{-5}	3 months	2.8–3.9	30–40 s	29.0	[49]
6	1×10^{-1} to 1×10^{-4}	4 months	2.8–4.2	30–40 s	28.5	[50]
7	1×10^{-1} to 1×10^{-5}	2 months	0.5–3.5	20–100 s	28.5	[51]
8	1×10^{-1} to 1×10^{-5}	2 months	0.5–2.5	20–100 s	29.6	[51]
9	1×10^{-1} to 5×10^{-5}	3 months	1.3–4.0	20 s	27.3	[52]
10	1×10^{-1} to 1×10^{-6}	3 months	4–9	40 s	30	Proposed assembly

of the Nernst plot during the experiment over a time period of 3 months. This suggests a longer electrode life and a stable electrode performance. The limit of detection of this electrode for the Hg(II) ions was obtained by extrapolating the linear curve of the standard calibration to the base line at 1×10^{-6} M. This is much lower than the detection limit usually obtained in the membrane based potentiometric sensors.

A comparison of the present Hg^{2+}-ISEs with those already reported in the literature is given in Table 6. From Table 6, it is clear that the performance of the proposed mercury(II) ion-selective membrane electrode based on the organic–inorganic composite cation-exchanger polyaniline Sn(IV) phosphate is comparable and better in many respects, such as the slope, response time, linear concentration range, life time, pH range and selectivity.

The response of this membrane electrode was also significantly affected by pH. As evident from Fig. 4, the electrode potential remained unchanged within a pH range of 4–9. After that pH, the electrode behaved in an erratic manner, which may be because mercury ions formed a hydroxyl complex and precipitated. Thus, we can say that the optimum pH range of operation of this electrode was pH 4–9. The selectivity coefficients, $K^{POT}_{Hg,M}$ of various cations for the Hg(II) ion-selective polyaniline Sn(IV) phosphate membrane electrode at pH 4 were determined by the mixed solution method [44], and the results are summarized in Table 7. It is seen from the Fig. 5 that alkali and alkaline earth metal ions do not interfere with the determination of mercury ions, while Cu(II), Zn(II), Pb(II) and Mn(II) interfere to a very little extent, and the interference of Fe(III) and Al(III was found to be negligible. Thus, the results revealed that th electrode was selective for Hg(II) in the presence of interferin cations.

Table 7
The selectivity coefficients, $K^{POT}_{Hg,M}$ of various interfering ions (M^{n+})

M^{n+}	$K^{POT}_{Hg,M}$
Na^{+}	$5 \times 10^{-}$
K^{+}	$5 \times 10^{-}$
Mg^{2+}	$5 \times 10^{-}$
Ca^{2+}	$1 \times 10^{-}$
Sr^{2+}	$1 \times 10^{-}$
Fe^{3+}	$5 \times 10^{-}$
Al^{3+}	$5 \times 10^{-}$
Cu^{2+}	$1 \times 10^{-}$
Zn^{2+}	$1 \times 10^{-}$
Pb^{2+}	$1 \times 10^{-}$
Mn^{2+}	$1 \times 10^{-}$

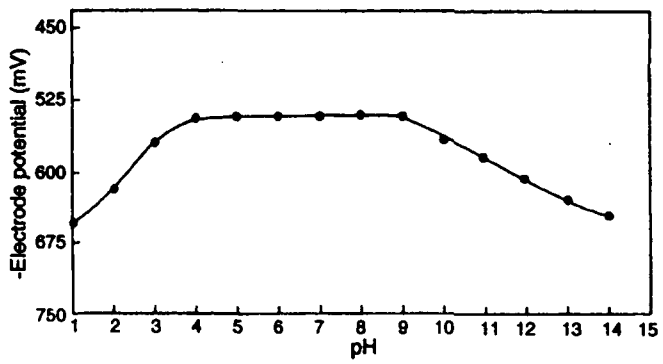

Fig. 4. Effect of pH on electrode response of Hg^{2+} ion-selective polyaniline Sn(IV) phosphate membrane electrode.

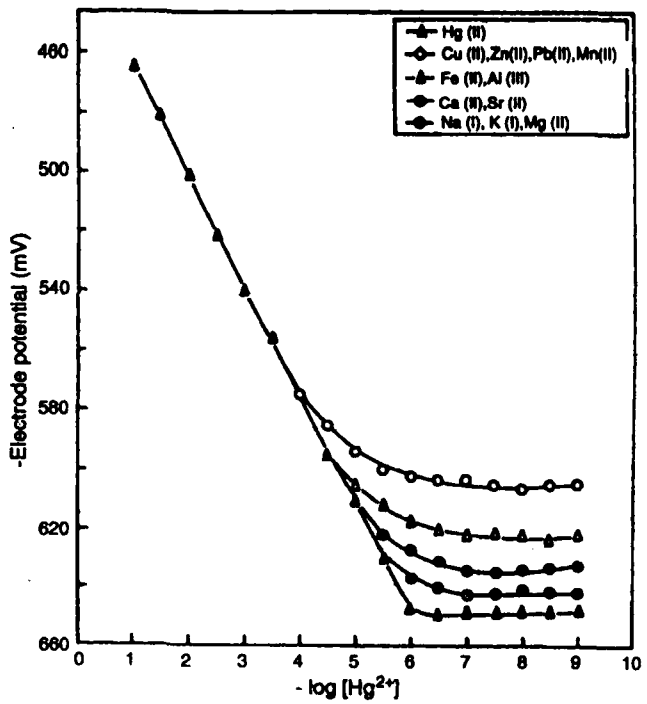

Fig. 5. Selectivity coefficients of various interfering ions for polyaniline Sn(IV phosphate PVC membrane electrode.

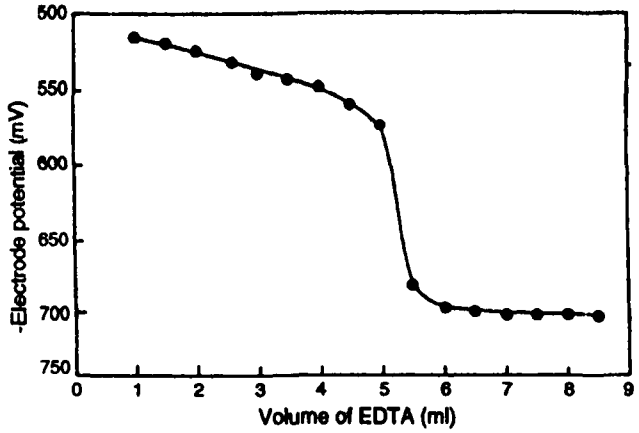

Fig. 6. Precipitation titration of Hg(II) against EDTA solution.

The analytical utility of this membrane electrode has been established by employing it as an indicator electrode in the potentiometeric titration of a 0.01 M $Hg(NO_3)_2$ solution against an EDTA solution as a titrant. The results are shown in Fig. 6. A 5 ml $Hg(NO_3)_2$ solution was pippeted out in a beaker, and its volume was raised up to 20 ml by adding demineralized water. This solution was titrated against an EDTA solution; the electrode potential was measured after each addition of 0.5 ml. The necessary adjustment of pH (≈4) was made before adding the titrant. The addition of EDTA causes a decrease in potential as a result of the decrease in free Hg(II) ion concentration due to formation of a complex with EDTA. The amount of Hg(II) ions in solutions can be accurately determined from the resulting neat titration curve providing a sharp end point. The potentiometric titration of Hg(II) was also successfully carried out in the presence of 1×10^{-5} M Ni(II), Cu(II) and Zn(II), hence demonstrating its applications as a sensor developed for potentmetric determination of Hg(II) in mixtures.

4. Conclusions

A polyaniline Sn(IV) phosphate cation-exchange material was found selective for Hg(II) ions. The membrane electrode of polyanline Sn(IV) exhibited a high sensitivity, selectivity and fast potential response to Hg(II) ions. The membrane electrode could be used to determine Hg^{2+} ions in the concentration range of 1×10^{-1} to 1×10^{-6} M and the pH range of 4–9. It showed good reproducibility, detection limit and lifetime of 3 months. It was found selective towards Hg^{2+} over other cations. It could also be used in the potentiometric titration of mercury ions.

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Preparation, physico-chemical characterization, analytical applications and electrical conductivity measurement studies of an 'organic–inorganic' composite cation-exchanger: Polyaniline Sn(IV) phosphate

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Abstract

Polyaniline Sn(IV) phosphate, an 'organic–inorganic' composite material, was synthesized via sol–gel mixing of an electrically conducting organic polymer polyaniline into the matrices of inorganic precipitate of Sn(IV) phosphate. This material was used as a cation-exchanger. The physico-chemical properties of the material were determined using AAS, CHN elemental analysis, ICP-MS, UV–VIS spectrophotometry, FTIR, TGA–DTA, XRD, and SEM studies. Ion-exchange capacity, chemical stability, thermal stability and distribution behavior were also carried out to understand the cation-exchange behavior of the material. On the basis of distribution studies, the material was found to be highly selective for Pb(II). Its selectivity was examined by achieving some important binary separations like Pb(II)–Mg(II), Pb(II)–Sr(II), Pb(II)–Zn(II), and Pb(II)–Fe(III) on its column. This material possessed DC electrical conductivity in the semi-conducting range, *i.e.* 10^{-5}–10^{-3} S cm^{-1}. The stability in terms of DC electrical conductivity retention was also studied in an oxidative environment by two slightly different techniques *viz.* isothermal and cyclic techniques. The DC electrical conductivity of composite material was found stable upto 110 °C under ambient conditions.

Keywords: Organic–inorganic composite material; Cation-exchanger; Electrical conductivity; Stability in terms of DC electrical conductivity retention; Polyaniline Sn(IV) phosphate

1. Introduction

A new class of high performance and high functional 'organic inorganic' electrically conducting composite ion-exchangers have been developed by the incorporation of organic conducting polymers into inorganic precipitates of polyvalent metal acid salts [1–3]. These materials were found selective for heavy toxic metal ions and utilized for analysis of water pollution. Such materials have great deal of attention because of their special mechanical, chemical, and electrochemical properties [4–6]. In the past

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few years, researchers have shown much interest in the study of electrically conducting behavior of 'organic–inorganic' composite materials [2,7–11]. Special interest today is focused on composite system having high conductivity at ambient and sub-ambient temperatures, since they find unique applications such as separators in high power and rechargeable lithium batteries. Moreover, composite materials composed of oxides or polyvalent metal acid salts and conducting polymers have brought out more fields of applications, such as smart windows, toners in photocopying, and conducting paints [12–14]. In the present research work, we have studied the synthesis, characterization, ion-exchange behavior and electrical conductivity measurement of a composite cation-exchanger 'polyaniline Sn(IV) phosphate' prepared by the incorporation of conducting polymer, *i.e.* polyaniline, into the matrices of inorganic ion-exchanger Sn(IV) phosphate.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, GSC, E-merck, Qualigens (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), an FTIR spectrophotometer (Perkin Elmer Spectrum-BX, USA), an automatic thermal analyzer (V2.2A Du Pont 9900), a Bruker AXS based X-ray diffractometer (Germany), an elemental analyzer (Carlo-Erba 1180), a double beam atomic absorption spectrophotometer (GBC 902, Australia), an inductively coupled plasma mass spectrophotometer, an electron microscope (LEO 435 VP, Australia) with attached imaging device, a digital flame photometer (Elico CL 22D, India), an UV/VIS spectrophotometer (Elico EI 301E, India), a water bath incubator shaker, and a four-in-line probe DC electrical conductivity-measuring instrument (Scientific Equipment, India) were used.

2.2. Preparation of reagents

A solution (0.1 M) of stannic chloride, $SnCl_4 \cdot 5H_2O$, was prepared in 4 M HCl, while 0.1 M di-sodium hydrogen orthophosphate, Na_2HPO_4 solution was prepared in demineralized water (DMW). Solutions of 10% (v/v) doubly distilled aniline ($C_6H_5NH_2$) and 0.1 M potassium persulphate ($K_2S_2O_8$) solution were prepared in 1 M HCl.

2.3. Preparation of polyaniline Sn(IV) phosphate

Polyaniline gels were prepared by mixing different volumes of the solutions of 10% aniline ($C_6H_5NH_2$) and 0.1 M potassium persulphate with continuous stirring by a magnetic stirrer. Green colored polyaniline gels were obtained by keeping the solutions below 10 °C for half an hour. A precipitate of Sn(IV) phosphate was prepared at room temperature (25 ± 2 °C) by adding 0.1 M stannic chloride solution to an aqueous solution of 0.1 M di-sodium hydrogen orthophosphate (Na_2HPO_4) in different volume ratios. The white precipitates were obtained, when the pH of the mixtures was adjusted to 1 by adding aqueous ammonia with constant stirring. The gels of polyaniline were added to the white inorganic precipitate of Sn(IV) phosphate and mixed thoroughly with constant stirring. The resultant green colored gels were kept for 24 h at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was decanted and the gel was filtered by suction. The excess acid was removed by washing with DMW and the material was dried in an air oven at 50 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H^+-form by treating with 1 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW and then dried at 50 °C. The particles size of the range (~125 μm) of materials was obtained by sieving and kept in desiccators. Hence, a number of samples of 'polyaniline Sn(IV) phosphate' composite cation-exchanger were prepared (Table 1) and on the basis of Na^+ ion-exchange capacity, the percentage of yield and the physical appearance of beads of sample S-7 was selected for detailed studies.

2.4. Ion-exchange capacity

One gram (1 g) of the dry cation-exchanger, sample S-7, in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~1 cm and fitted with a glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1 M alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard (0.1 M) NaOH solution using phenolphthalein indicator and the

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Table 1
Conditions of preparation of various samples of polyaniline Sn(IV) phosphate composite cation-exchange material

Samples	Mixing volume ratio					Appearance of beads after drying	Na^+ ion-exchange capacity (meq dry g^{-1})
	0.1 M $SnCl_4 \cdot 5H_2O$ in 4 M HCl	0.1 M Na_2HPO_4 in DMW	pH of the inorganic precipitate	0.1 M $K_2S_2O_8$ in 1 M HCl	10% Aniline in 1 M HCl		
S-1	1	1	1.0	1	1	Greenish granular	1.10
S-2	1	2	1.0	1	1	Greenish granular	1.45
S-3	2	1	1.0	1	1	Greenish granular	0.85
S-4	2	2	1.0	1	1	Greenish granular	0.96
S-5	–	–	–	1	1	Greenish granular	0.20
S-6	2	3	1.0	–	–	White granular	1.12
S-7	2	3	1.0	1	1	Greenish granular	1.96
S-8	1	3	1.0	1	1	Greenish granular	0.58
S-9	1	4	1.0	1	1	Greenish granular	0.45
S-10	3	4	1.0	1	1	Greenish granular	0.72
S-11	2	3	1.0	2	1	Greenish granular	1.20
S-12	2	3	1.0	1	2	Dark green	0.98
S-13	2	3	1.0	2	2	Greenish granular	1.40
S-14	2	3	1.0	3	2	Greenish granular	0.92
S-15	2	3	1.0	2	3	Greenish granular	0.85

ion-exchange capacities (I.E.C.) in meq g^{-1} are given in Table 2.

2.5. Thermal effect on ion-exchange capacity (I.E.C.)

To study the effect of drying temperature on the I.E.C., 1 g samples of the composite cation-exchange materials (S-7) in the H^+-form were heated at various temperatures in a muffle furnace for 1 hour and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature (Table 3).

2.6. Effect of eluant concentration

To find out the optimum concentration of the eluant for complete elution of H^+ ions, a fixed volume (250 ml) of $NaNO_3$ solution of varying concentrations was passed through a column containing 1 g of the exchanger in the H^+-form with a flow rate of ~0.5 ml min^{-1}. The effluent was titrated against a standard alkali solution of 0.1 M NaOH for the H^+ ions eluted out. A maximum elution was observed with the concentration of 1 M $NaNO_3$ as indicated in Fig. 1.

2.7. Elution behavior

Since an optimum concentration of 1 M $NaNO_3$ for a complete elution of H^+ ions was observed for sample S-7 (Fig. 1), a column containing 1 g of the cation-exchanger in H^+-form was eluted with $NaNO_3$ solution of this concentration in different 10 ml fractions with minimum flow rate as described above. Each fraction of 10 ml effluent was titrated against a standard alkali solution for the H^+ ions eluted out (Fig. 2).

Table 2
Ion-exchange capacity of various exchanging ions on polyaniline Sn(IV) phosphate cation exchanger

Exchanging ions	pH of the metal solutions	Ionic radii (Å)	Hydrated ionic radii (Å)	I.E.C. (meq dry g^{-1})	
				H^+-liberation	H^+-adsorption
Li^+	6.7	0.68	3.40	1.43	1.41
Na^+	6.7	0.97	2.76	1.96	1.82
K^+	6.8	1.33	2.32	2.07	2.09
Mg^{2+}	6.5	0.78	7.00	2.05	2.03
Ca^{2+}	6.5	1.06	6.30	2.15	2.16
Sr^{2+}	6.3	1.27	–	2.26	2.29
Ba^{2+}	6.3	1.43	5.90	2.32	2.33

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Table 3
Effect of temperature on ion-exchange capacity of polyaniline Sn(IV) phosphate cation-exchanger on heating time for 1 hour

Heating temperature (°C)	Appearance (Color)	Weight loss (%)	Na^+ ion-exchange capacity (meq dry g^{-1})	% Retention of I.E.C.
40	Greenish granular	–	1.96	100
100	Greenish granular	8.60	1.96	100
150	Greenish granular	14.12	1.96	100
200	Greenish granular	16.50	1.71	87.12
300	Dark green	20.00	1.42	72.46
350	Black	22.13	1.16	59.31
400	Blackish brown	23.42	0.77	39.29
500	Slightly white	32.64	0.53	26.94
600	White	34	0.22	11.02

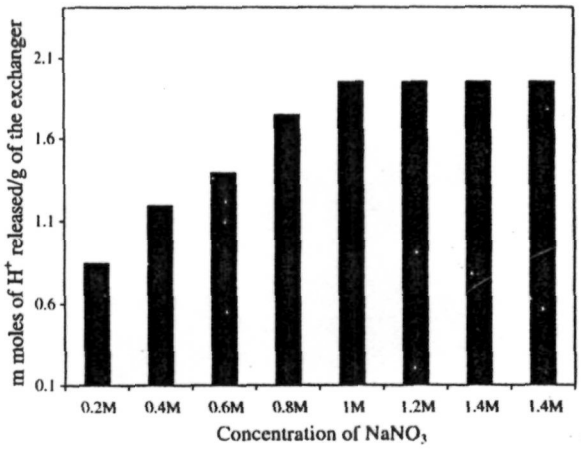

Fig. 1. Effect of eluent concentration on ion-exchange capacity of polyaniline Sn(IV) phosphate cation-exchanger.

2.8. Chemical composition

To determine the chemical composition of 'polyaniline Sn(IV) phosphate' (Sample S-7), 200 mg of the sample was dissolved in 20 ml of concentrated H_2SO_4. The material was analyzed for 'Sn(IV)' by ICP-MS and phosphate by the phosphovanado molybdate method [15]. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The weight percent composition of the material was Sn, 17.2; P, 14.25; C, 10.08; H, 3.46; N, 2.06; O, 52.95.

2.9. Chemical dissolution

Two hundred mg portions of the sample (S-7) were treated with 20 ml each of different acids,

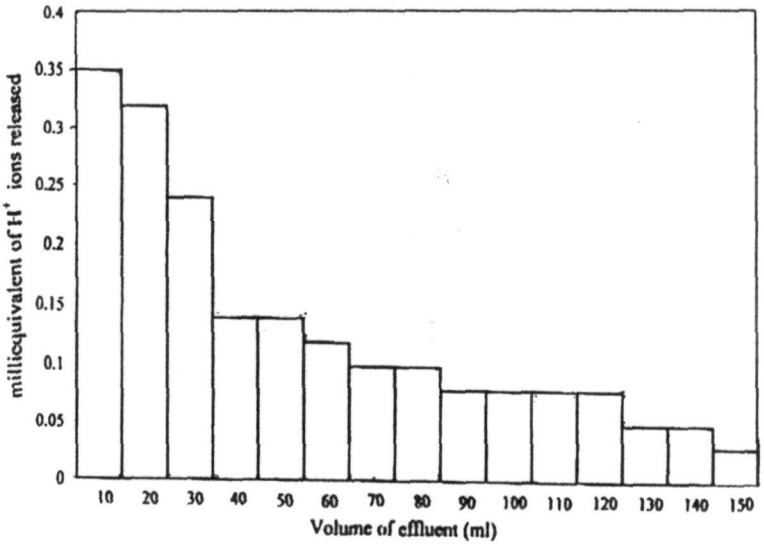

Fig. 2. Elution behavior of polyaniline Sn(IV) phosphate cation-exchange material.

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Table 4
Chemical stability of polyaniline Sn(IV) phosphate in various solvents

Solvent used (20 ml)	Amount dissolved (mg/20 ml)	
	Sn(IV)	Phosphorus
DMW	0.00	0.150
1 M HCl	0.04	0.965
2 M HCl	0.04	1.542
4 M HCl	0.04	1.672
1 M HNO_3	0.04	0.930
2 M HNO_3	0.04	1.333
4 M HNO_3	0.34	1.546
1 M H_2SO_4	0.05	0.863
2 M H_2SO_4	0.05	0.425
4 M H_2SO_4	0.06	0.841
1 M formic acid	0.06	1.942
1 M citric acid	0.05	0.756
1 M CH_3COOH	0.05	1.347
0.1 M KOH	0.00	1.020
0.1 M NaOH	0.00	0.783
1 M CH_3COONa	0.00	0.312
1 M NH_4NO_3	0.02	0.985
10% dimethyl sulphoxide (DMSO)	0.11	1.860
Acetone	0.05	0.512
n-Butyl alcohol	0.07	1.423

bases, organic solvents, salts, etc. for 24 h with intermittent shaking. The supernatant liquid was analyzed for Sn(IV) by atomic absorption spectrometer, while phosphate was determined as usual by the phosphovanado molybdate method [15]. The results are summarized in Table 4.

2.10. Thermogravimetric analysis-differential thermal analysis (TGA–DTA) studies

Simultaneous TGA–DTA studies were also carried out on heating the sample material S-7 (as-prepared) up to 900 °C at a constant rate (~10 °C min^{-1}) in the air atmosphere. Fig. 3 shows the TGA–DTA curves of the cation-exchange material.

2.11. FTIR studies

The FTIR spectrum of polyaniline (S-5), Sn(IV) phosphate (S-6) and polyaniline Sn(IV) phosphate (S-7) (as-prepared) dried at 50 °C was taken by KBr disc method and is shown in Fig. 4.

2.12. X-ray studies

Powder X-ray diffraction pattern of the material S-7 (as-prepared) was recorded by a Bruker AXS based diffractometer with Cu Kα radiation and is shown in Fig. 5.

2.13. Scanning electron microscopy studies

SEM was performed on ground materials (as prepared) by an electron microscope at various magnifications. Fig. 6 represents the microphotographs of samples S-5, S-6, and S-7.

2.14. Electrical conductivity measurements

An electrically conducting composite cation-exchanger 'polyaniline Sn(IV) phosphate' (S-7) was treated with 0.5 M aqueous HCl and washed for excess HCl with distilled water repeatedly until the filtrate was at neutral pH. Then the material (0.5 g) was finally ground in a mortar pestle and a pellet was made at room temperature with the help of a hydraulic pressure instrument at 25 kN pres-

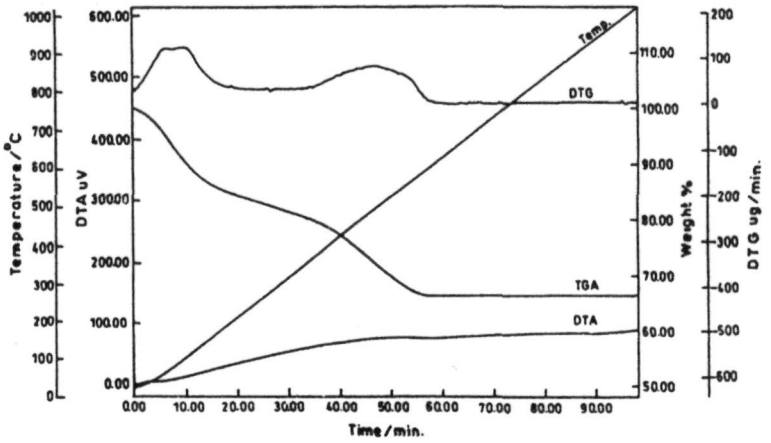

Fig. 3. Simultaneous TGA–DTA curves of polyaniline Sn(IV) phosphate (as-prepared).

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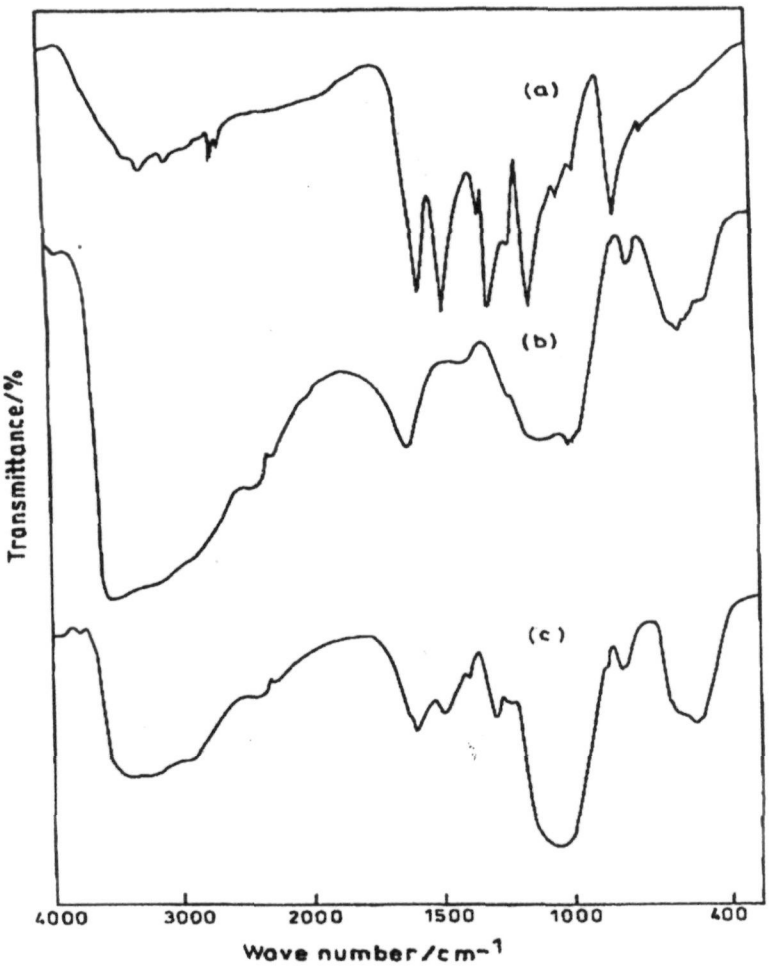

Fig. 4. FTIR spectra of as prepared polyaniline (a), Sn(IV) phosphate (b), and polyaniline Sn(IV) phosphate composite material (c).

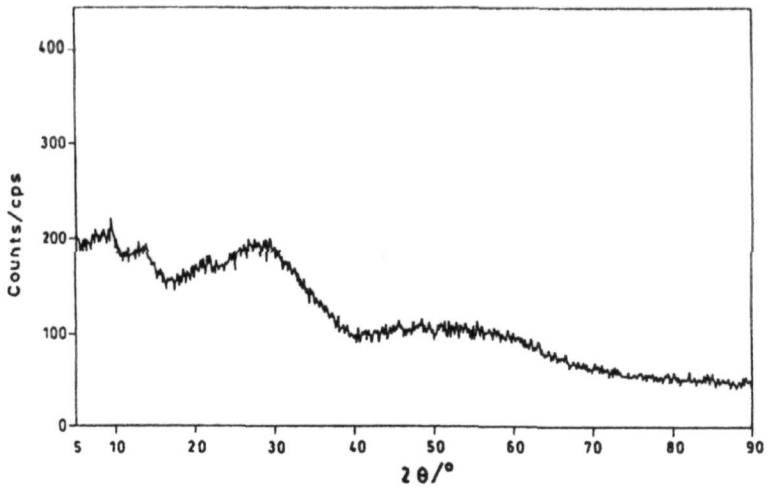

Fig. 5. Powder X-ray diffraction pattern of polyaniline Sn(IV) phosphate (as prepared).

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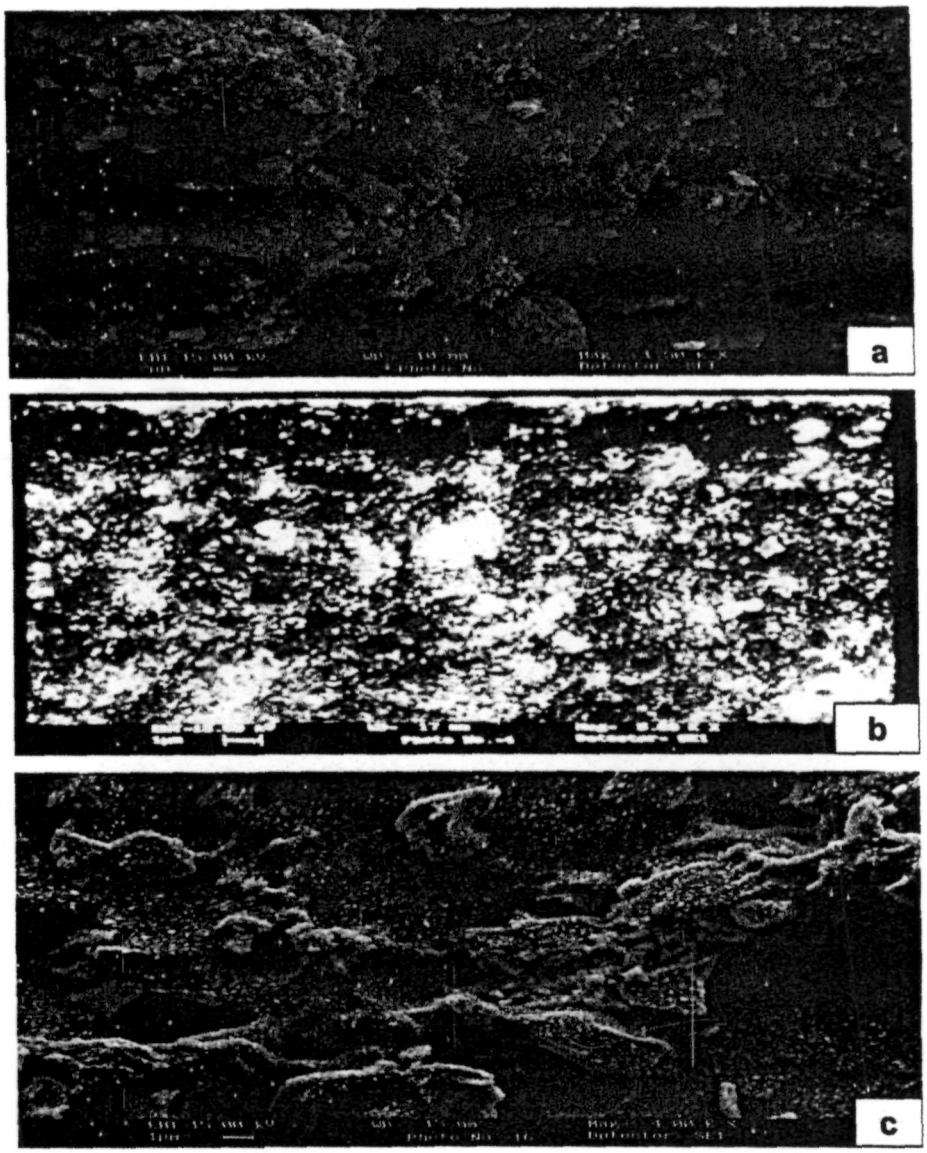

Fig. 6. Scanning electron microphotographs (SEM) of chemically prepared polyaniline at the magnification of 1500× (a), Sn(IV) phosphate at the magnification of 5000× and (b) polyaniline Sn(IV) phosphate composite system at the magnification of 4000× (c).

sure for 20 min. The thickness of the pellet was measured by a micrometer.

Four probe DC electrical conductivity measurements with increasing temperature for the representative sample (S-7) (as prepared and HCl treated) were performed on pressed pellets by using a four-in-line-probe DC electrical conductivity measuring technique. The sample to be tested was placed on the base plate of four-probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure was applied on the probes and then it was tightened in this position so as to avoid piercing of the probes into the samples. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of the probes was measured. The oven supply is then switched on, the temperature was allowed to increase gradually while current and voltage were recorded with rise in temperatures.

The current -voltage data so generated by a four-in-line probe DC electrical conductivity-measuring instrument was processed for calculation of resistivity (ρ_0) using the following equation:

$$\rho_0 = (V/I) \times 2\pi S \quad (1)$$

where V is the voltage (V) and I is the current (A).

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Since the thickness of the sample is small compared to the probe distance, a correction factor for it has to be applied and the corrected resistivity may be calculated as:

$$\rho = \rho_0 / G_7(W/S) \quad (2)$$

where ρ is the corrected resistivity in ohm cm, $G_7(W/S)$ is the correction factor used in the case of non-conducting bottom surface and the function W is the thickness of the sample under test (cm) and S, the probe spacing (cm); *i.e.*,

$$G_7(W/S) = (2S/W)\log_e 2 \quad (3)$$

Thus, the electrical conductivity (σ) was calculated using the following equation:

$$\sigma = 1/\rho \quad (4)$$

where σ is the electrical conductivity in S cm^{-1}.

This composite material was also treated with 0.5 M NaCl, LiCl, $CaCl_2$, $Pb(NO_3)_2$, $MnCl_2$, and $Cu(NO_3)_2$ solutions, and electrical conductivity measurements were carried out on these different forms (Na^+, Li^+, Ca^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}) of composite cation-exchangers.

The isothermal stability of polyaniline Sn(IV) phosphate composite in terms of DC electrical conductivity retention was carried out on the selected samples (treated with 0.5 M HCl) at 50 °C, 70 °C, 90 °C, 110 °C and 130 °C in an air oven. The electrical conductivity measurements were carried out at an interval of 15 min. The thermal stability of the composite material in terms of DC electrical conductivity retention was also studied by a cyclic measurement of the DC electrical conductivity on pressed pallets with increasing temperature from 30 °C to 200 °C. The measurements were repeated on the same sample in this temperature range for five times at intervals of 45 min.

2.15. Distribution (sorption) studies

The distribution coefficients (K_d values) of various metal ions on polyaniline Sn(IV) phosphate were determined by batch method in various solvent systems. Various composite cation-exchanger beads (S-7) of 200 mg in the H^+ ion form were taken in Erlenmeyer flasks with 20 ml of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion concentration was to adjust such that it does not exceed 3% of its total ion exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.005 M solution of EDTA [16] and some heavy metal ions such as [Pb^{2+}, Hg^{2+}, Zn^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution coefficient (K_d) values were calculated using the formula given below:

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \text{ ml g}^{-1} \quad (4)$$

where I is the initial amount of the metal ion in the solution phase, F is the final amount of the metal ion in the solution phase, V is the volume of the solution (ml), and M is the amount of the exchanger (g).

2.16. Quantitative separation of metal ions

Quantitative binary separations of some important metal ions of analytical utility were achieved on polyaniline Sn(IV) phosphate column. 1 g of the cation-exchanger, S-7 (~125 μm) in H^+-form was used for column separations in a glass tube having an internal diameter of ~0.6 cm and a height of 35 cm. The column was washed thoroughly with DMW and the mixture of two metal ions having initial concentrations of 0.01 M each, to be separated, was loaded on it and allowed for 1 h to absorb the metal ions on the exchanger and pass on to the column gently (maintaining a flow rate of 2–3 drops per minute) till the level was above the surface of the material. After recycling two or three times to ensure complete absorption of the mixture on column beads, the separation was achieved by passing a suitable solvent at a flow rate of 1 ml min^{-1} through the column as eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration.

3. Results and discussion

In this study of the preparation and characterization of 'organic–inorganic' composite cation-exchange material, a number of samples of 'organic–inorganic' electrically conducting composite polyaniline Sn(IV) phosphate providing a new class of hybrid ion-exchangers were prepared by the sol–gel mixing of organic conducting polymer polyaniline into the inorganic precipitate of Sn(IV) phosphate (Table 1). Among them, sample S-7 pos-

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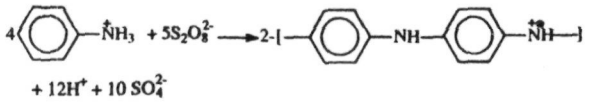
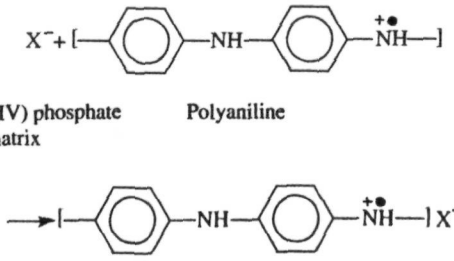
sessed better Na^+ ion-exchange capacity (1.96 meq dry g^{-1}) as compared to Sn(IV) phosphate (1.12 meq dry g^{-1}), high percentage of yields, chemical, mechanical, and thermal stabilities.

Polyaniline gel was prepared by oxidative coupling using $K_2S_2O_8$ in acidic aqueous medium [17] as given in the following reaction:



The effect of temperature on the reaction seems to be very pronounced. Aniline underwent oxidative coupling only below 10 °C very effectively, leading to a good quantity of polyaniline with fairly good yield. The formation of inorganic precipitate of polyaniline Sn(IV) phosphate was significantly affected by the pH and the most favorable pH of the mixture was ~1.0. The binding of polyaniline into the matrix of Sn(IV) phosphate can be as:



However, sample S-7 of polyaniline Sn(IV) phosphate exhibited granulometric and mechanical properties, showing a good reproducible behavior as is evident from the fact that these materials obtained from various batches did not show any appreciable deviation in their percentage of yield and ion-exchange capacities. The effect of the size and charge of the exchanging ion on the ion-exchange capacity was also observed for this material. The ion-exchange capacity of the composite cation-exchanger for alkali ions and alkaline earth metal ions increases according to the decrease in the hydrated ionic radii (Table 2). It was also found that the values of H^+-adsorption and H^+-liberation capacities are in close agreement (Table 2).

It was observed that on heating at different temperatures for 1 h, the mass, physical appearance and ion-exchange capacity of the dried sample material (S-7) were changed as the temperature increased as shown in Table 3. The material was found to possess higher thermal stability as the sample maintained about 67% of the initial mass by heating up to 500 °C. However, in respect to ion-exchange capacity, this material was found stable up to 150 °C and it retains about 59% of the initial ion-exchange capacity by heating up to 350 °C. A comparative study of heating effect on Na^+ ion-exchange capacity of polyaniline Sn(IV) phosphate with those of other ion-exchangers of this class is shown in Fig. 7. It is clear that this composite cation-exchanger is more thermally stable than others.

The column elution experiment indicated a dependence of the concentration of the eluent on the rate of elution, which is an usual behavior, for such materials. The minimum molar concentration of $NaNO_3$ as an eluent for sample S-7 was 1 M for maximum release of H^+ ions from 1 g of the cation-exchanger as is evident from Fig. 1. The elution behavior indicates that the exchange is quite fast at the beginning as all the exchangeable H^+ ions are eluted out in the first 150 ml of the effluent (Fig. 2) from a column of 1 g exchanger within 5 h.

The solubility experiment (Table 4) showed that the material has reasonable good chemical stability as the results indicated that the material was resistant to solutions of different acids, bases, organic solvents, salts, etc. The chemical dissolution in DMW, alkaline media, CH_3COONa, NH_4NO_3, was almost negligible. The chemical stability may be due to the presence of binding polymer, which can prevent the

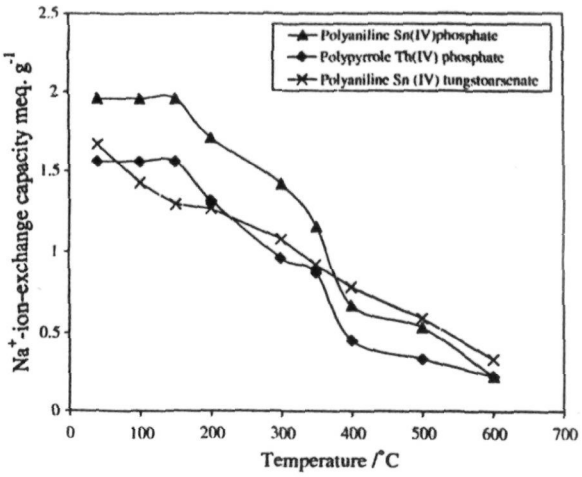


Fig. 7. Comparison of heating effect upon ion-exchange capacity of polyaniline Sn(IV) phosphate composite cation-exchanger.

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dissolution of heteropolyacids sols or leaching of any constituent element into the solution.

The TGA–DTA analysis curve (Fig. 3) of the polyaniline Sn(IV) phosphate showed continuous weight loss of mass (about 12%) upto 135 °C, which may be due to the removal of external water molecule [18]. A slow weight loss (~9.02%) observed between 135 °C and 398 °C may be due to the condensation of phosphate group to pyrophosphate groups. Further weight loss (~12.03%) between 398 °C and 601 °C may be due to the complete decomposition of the organic part of the material. From 601 °C onwards, a smooth horizontal section represents the complete formation of the oxide form of the material. The weight loss percent with increasing temperatures observed by TGA curve is also supported by the thermal stability experiment (Table 3).

Fig. 4 shows the FTIR spectrum of polyaniline (a), Sn(IV) phosphate (b), and polyaniline Sn(IV) phosphate (c). It is evident from the FTIR studies of the 'organic–inorganic' composite cation-exchanger in H^+-form sample S-7 (Fig. 4c) that the material shows the presence of external water molecule in addition to –OH groups and the metal oxygen bond. In the spectrum of the material, a strong and broad band around 3400 cm^{-1} is found which can be ascribed to –OH stretching frequency. A sharp peak around 1600 cm^{-1} can be attributed to H–O–H bending band, which represents the strongly bonded –OH groups in the matrix [19]. The –OH stretching bands merge together and shift to lower frequency in the spectrum of the composite cation-exchanger. A strong and broad band around 1000 cm^{-1} may represent the presence of ionic phosphate groups [20]. An assembly of two sharp peaks in the region 500–800 cm^{-1} may be due to the presence of metal oxygen bond [21,22].

In the sample of Sn(IV) phosphate (Fig. 4b), there is a very strong and very broad –OH stretching band around 3500 cm^{-1} region and two very strong bands around 800 cm^{-1} and 1000 cm^{-1} regions are due to the presence of Sn–O stretching frequency and ionic phosphate groups, respectively. These characteristic stretching frequencies show close resemblance with the inorganic precipitate, *i.e.* tin(IV) phosphate (Fig. 4b) and polyaniline Sn(IV) phosphate (Fig. 4c), indicating the binding of inorganic precipitate with organic polymer and formation of 'organic–inorganic' composite 'polyaniline Sn(IV) phosphate.' Another assembly of two peaks in the region 1300–1400 cm^{-1} may be ascribed due to the stretching vibration frequency of C–N [23] in the material (Fig. 4c), as it also resembles the stretching vibration frequencies for C–N found in polyaniline (Fig. 4a). This indicates that the polyaniline Sn(IV) phosphate contains considerable amount of aniline.

X-ray diffraction pattern of this composite cation-exchanger (sample S-7 as prepared) shows very small peaks of 2θ values. The analysis of these small signal peaks supports towards its semi-crystalline nature (Fig. 5). Scanning electron microscope (SEM) photographs of polyaniline, Sn(IV) phosphate and polyaniline Sn(IV) phosphate obtained at different magnifications (Fig. 6) indicate the binding of inorganic ion-exchange material with organic polymer, *i.e.* polyaniline. The SEM pictures show the difference in surface morphology of organic polymer, inorganic precipitate and composite material. It has been revealed that after binding of polyaniline with Sn(IV) phosphate, the morphology has been changed.

The molar ratio of Sn, P, C, H, N, and O in the material was estimated as 1:3.28:6:24.50:1.07:23.57, which can suggest the following formula of the material:

$$[(SnO_2)(H_3PO_4)_3 \cdot (\text{-}C_6H_4NH\text{-})] \cdot nH_2O.$$

Assuming that only the external water molecules are lost at 135 °C and ~12.42% weight loss of mass represented by TGA curve must be due to the loss of nH_2O from the above structure, the value of 'n' the external water molecules can be calculated using Alberti's equation [24]:

Table 5
Values of DC electrical conductivity for the polyaniline and polyaniline Sn(IV) phosphate composite with different concentrations of aniline monomer

Samples	Ambient temperature DC electrical conductivity (S cm^{-1})					
Polyaniline	9.12×10^{-4}					
Polyaniline Sn(IV) phosphate composite	Aniline monomer concentration (vol.%)					
	6%	8%	10%	12%	14%	16%
	9.46×10^{-5}	2.54×10^{-4}	5.23×10^{-3}	6.48×10^{-3}	6.93×10^{-3}	8.01×10^{-3}

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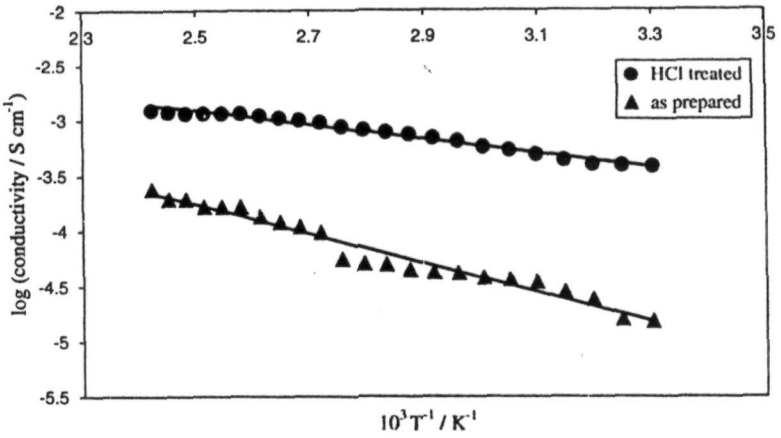

Fig. 8. Arrhenius plots for polyaniline Sn(IV) phosphate composite material.

Table 6
Four-probe DC electrical conductivity of different forms of polyaniline Sn(IV) phosphate composite systems at ambient temperature (prepared with 10% aniline monomer)

Samples	Polyaniline Sn(IV) phosphate	Ambient temperature DC electrical conductivity (S cm^{-1})
1.	As prepared	2.39×10^{-4}
2.	HCl treated	5.85×10^{-3}
3.	NaCl treated	3.32×10^{-5}
4.	KCl treated	2.21×10^{-5}
5.	LiCl treated	1.41×10^{-5}
6.	$CaCl_2$ treated	1.06×10^{-5}
7.	$Pb(NO_3)_2$ treated	4.82×10^{-8}
8.	$MnCl_2$ treated	3.24×10^{-8}
9.	$Cu(NO_3)_2$ treated	6.24×10^{-8}

$$18n = X(M + 18n)/100 \quad (5)$$

where X is the percent weight loss (~12%) of the exchanger by heating up to 135 °C and $(M + 18n)$ is the molecular weight of the material. The calculations give ~5 for the external water molecule (n) per molecule of the cation-exchanger (sample S-7).

The main constituent that makes the composite electrically conductive is polyaniline when present in sufficient amount. The conducting properties depend on the percolation behavior of the conducting phase. Therefore, the dependence of the electrical conductivity with different concentrations of aniline monomer was examined (Table 5). On examination, it was observed that the slight increase in

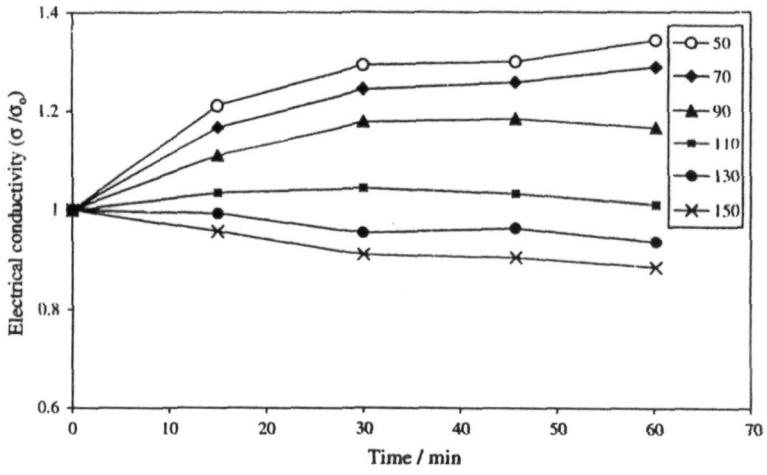

Fig. 9. Isothermal stability of polyaniline Sn(IV) phosphate composite (HCl treated) in terms of retention of DC electrical conductivity with respect to time at 50 °C, 70 °C, 90 °C, 110 °C, 130 °C, and 150 °C.

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electrical conductivity for the composites was followed at a certain aniline concentration by a sudden jump, which was again followed by a moderate increase. At about 8% aniline concentration (critical concentration of conducting phase), this sharp rise in electrical conductivity is observed and could possibly be explained on the basis of percolation theory [25].

The electrical conductivity (σ) measurements of the composite cation-exchanger (as prepared and 0.5 M HCl treated) were observed with increasing temperatures from 30 °C to 140 °C. To determine the nature of dependence of electrical conductivity on temperature, plots of $\log\sigma$ versus $1000/T$ (K) were drawn (Fig. 8) and they followed Arrhenius equation similar to other semi-conductors [26]. On examination, it was found that the composite material showed enhanced electrical conductivity on exposure to HCl, due to the charge-transfer reaction between polyaniline component of the composite and doping agent, HCl.

$$[\text{Polyaniline Sn(IV) phosphate}] + n\ \text{HCl} \rightarrow [\text{Polyaniline } (nH^+)(HCl^-)\ \text{Sn(IV) phosphate}] \quad (6)$$

It was also observed that the electrical conductivities of the composite materials (as prepared and 0.5 M HCl treated) increase with the increase in temperature and the values lie in the order of 10^{-5}–10^{-3} S cm^{-1}, *i.e.* in the semi-conductor region.

The effect on electrical conductivity of the different forms (Na^+, Li^+, Ca^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}), of composite cation-exchangers was also examined and is presented in Table 6. It was observed that the electrical conductivity was affected negligibly, when treated with the metal nitrate solutions of (Na^+, Li^+, Ca^{2+}, Cu^{2+}), while the electrical conductivity of Pb^{2+}, Cu^{2+}, Mn^{2+} forms was decreased to 10^{-8}, beyond the semi-conducting region (Table 6).

The thermal stability of the composite material (HCl treated) in terms of DC electrical conductivity retention was studied under isothermal conditions (at 50 °C, 70 °C, 90 °C, 110 °C, 130 °C, and 150 °C) using four-probe-in-line DC electrical conductivity measurements at 15 min intervals. The electrical conductivity measured with respect to the time of accelerated ageing is presented in Fig. 9. It was observed that the electrical conductivity is quite stable at 50 °C, 70 °C, 90 °C, and 110 °C, which supports the fact that the DC electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 °C and 150 °C, which may be due to the loss of dopant and the chemical reaction of dopant with the material.

The stability of the material (HCl treated) in terms of electrical conductivity retention was also monitored for five cycles by repeated linear four-probe DC electrical conductivity measurements for increasing temperatures at 45 min intervals, and

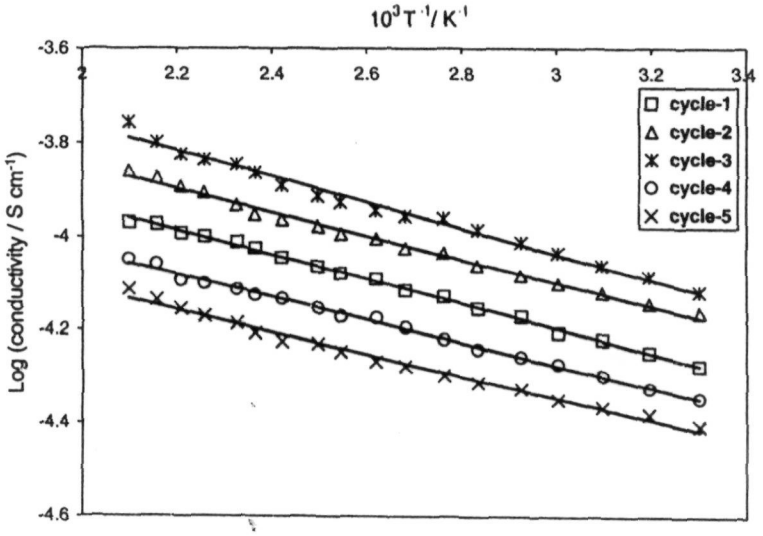

Fig. 10. Arrhenius plots of retention of DC electrical conductivity for polyaniline Sn(IV) phosphate (HCl treated) during heating cooling cycles up to 200 °C.

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the dc conductivity for each heating cycle was plotted as $\log\sigma$ versus $1000/T$ (T in K) as shown in Fig. 10. It was observed that the temperature dependence of each plot followed the Arrhenius equation. There were only minor differences in the electrical conductivities even after repeating the experiment five times, which showed the good stability of the material during the heating–cooling cycles under severe oxidizing conditions up to 200 °C. The material was also found stable to be at room temperature as the electrical conductivity at room temperature is negligibly affected by short-term exposure to laboratory air as is evident from Fig. 11.

In order to explore the potentiality of the composite cation-exchange material in the separation of metal ions, distribution studies for 12 metal ions were performed in ten solvent systems (Table 7). The distribution studies showed that the material was found to be highly selective for Pb(II).

The separation capability of the material has been demonstrated by achieving some important binary separations viz. Pb(II)–Mg(II), Pb(II)–Sr(II), Pb(II)–Zn(II), Pb(II)–Fe(III), etc. The salient features of these separations are summarized in Table 8. The separations are quite sharp and recoveries are quantitative and reproducible.

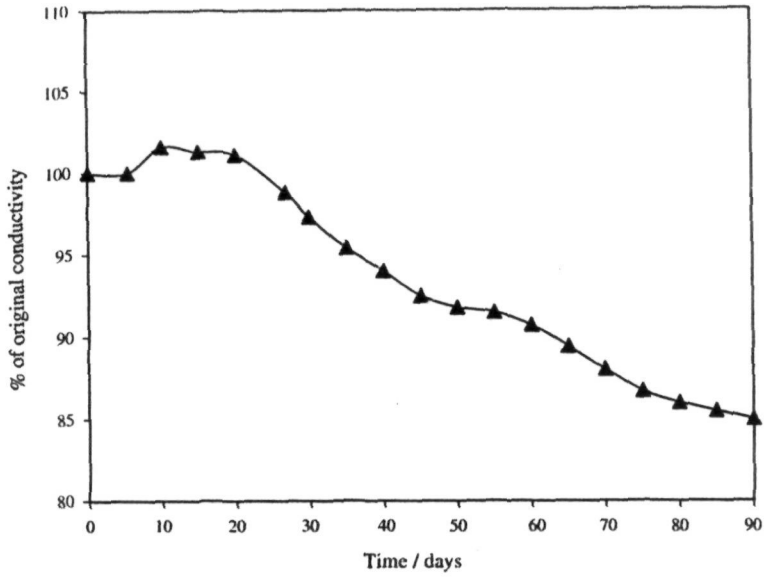

Fig. 11. Conductivity versus time of exposure to laboratory air for polyaniline Sn(IV) phosphate composite material (HCl treated).

Table 7
K_d-values of some metal ions on polyaniline Sn(IV) phosphate column in different solvent systems

Metal ions	DMW	10^{-3} M HNO_3	10^{-2} M HNO_3	10^{-1} M HNO_3	10^{-3} M HCl	10^{-2} M HCl	10^{-1} M HCl	0.1 M CH_3COOH + 0.1 M CH_3COONa (1:2)	0.1 M CH_3COOH + 0.1 M CH_3COONa (2:1)	0.1 M HNO_3 + 0.1 M NH_4NO_3 (1:1)
Na^+	125	151	200	215	300	120	300	96	54	85
K^+	212	285	321	145	167	200	185	175	158	64
Mg^{2+}	300	271	219	112	300	176	34	316	975	100
Ca^{2+}	141	141	83	34	123	844	46	200	753	371
Sr^{2+}	181	36	15	19	12	–	4	158	94	70
Ba^{2+}	79	48	39	27	225	133	–	113	333	112
Zn^{2+}	386	566	158	88	363	66	62	237	471	–
Pb^{2+}	2900	2800	2900	2311	2800	1400	250	1300	2200	210
Fe^{3+}	700	700	233	205	900	136	116	500	1300	58
Bi^{3+}	2300	1500	2000	2300	1400	–	–	650	1400	66
Tl^+	233	206	200	140	100	260	16	458	135	28
Ag^+	278	118	19	54	34	12	10	22	84	16

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Table 8
Some binary separation of metal ions achieved on polyaniline Sn(IV) phosphate composite cation exchanger

Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluent used	Volume of eluent (ml)
Mg(II)	850.66	849.45	−0.14	0.1 M HNO_3	60
Pb(II)	4144.00	4144.00	0.00	0.1 M HCl	50
Zn(II)	1307.40	1310.67	+0.25	0.1 M HCl	60
Pb(II)	3108.00	3097.64	−0.33	0.1 M HNO_3 + 0.1 M NH_4NO_3	50
Ba(II)	2059.5	20458.77	−0.67	0.1 M HNO_3	50
Pb(II)	4144.0	4133.64	−0.25	0.1 M HNO_3 + 0.1 M NH_4NO_3	50
Sr(II)	876.2	884.96	+0.99	0.1 M HCl	50
Pb(II)	3108.0	3108.00	0.00	0.1 MHNO_3 + 0.1 M NH_4NO_3	50
Bi(III)	2089.8	2110.70	+1.00	0.1 M CH_3COOH + 0.1 MCH_3COONa	50
Pb(II)	3626.00	3615.64	−0.27	0.1 MHNO_3 + 0.1 M NH_4NO_3	50
Fe(III)	1116.80	1111.23	−0.50	0.1 M HCl	50
Pb(II)	2590.00	2610.00	+0.77	0.1 MHNO_3 + 0.1 M NH_4NO_3	50

4. Conclusions

Polyaniline Sn(IV) phosphate organic–inorganic electrically conducting composite cation-exchange material represents a new class of ion-exchange materials that may combine physical properties and characteristics of both organic and inorganic components within a single composite. It is quite clear from the results that the composite cation-exchanger is a semi-conductor (conductivity lies in the range 10^{-5}–10^{-3} S cm^{-1}) and has enhanced ion-exchange capacity, high chemical, mechanical, and thermal stabilities. The selective behavior of this composite cation-exchanger is important from the environmental pollution chemistry point of view, where an effective separation method is needed for Pb(II) from other pollutants.

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Cation-Exchange Kinetics and Electrical Conductivity Studies of An 'Organic-Inorganic' Composite Cation-Exchanger: Polypyrrole Th(IV) Phosphate

AQ2 **Asif Ali Khan, Inamuddin**

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ABSTRACT: Polypyrrole Th(IV) phosphate, an electrically conducting 'organic-inorganic' cation-exchange composite material was prepared by the incorporation of an electrically conducting polymer, i.e., polypyrrole, into the matrix of a fibrous type inorganic cation-exchanger thorium(IV) phosphate. The composite cation-exchanger has been of interest because of its good ion-exchange capacity, higher chemical and thermal stability, and high selectivity for heavy metal ions. The temperature dependence of electrical conductivity of this composite system with increasing temperatures was measured on compressed pellets by using four-in-line-probe dc electrical conductivity measuring instrument. The conductivity values lie in the semiconducting region, i.e., in the order of 10^{-6} to 10^{-4} S cm^{-1} that follow the Arrhenius equation. Nernst–Plank equation has been applied to determine some kinetic parameters such as self-diffusion coefficient (D_0), energy of activation (E_a), and entropy of activation (ΔS^*) for Mg(II), Ca(II), Sr(II), Ba(II), Ni(II), Cu(II), Mn(II), and Zn(II) exchange with H^+ at different temperatures on this composite material. These results are useful for predicting the ion-exchange process occurring on the surface of this cation-exchanger. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2006

Key words: organic-inorganic composite material; cation-exchanger; electrical conductivity; ion-exchange kinetics

INTRODUCTION

The possibility of combining the properties of organic and inorganic compounds in a unique material is an old challenge. Actually, research on hybrid organic/inorganic materials is an expending area in the material science.[1–10] Therefore, organic-inorganic composite materials are of intensive interest in the field of contemporary materials chemistry as these materials can exhibit synergetic extraordinary properties such as electrical, magnetic, and optical properties,[11] which arise from the synergism between the properties of the organic and inorganic components. Thus, these materials have gained much interest because of their remarkable change in properties such as mechanical,[12] thermal,[13–16] electrical,[17] and magnetic[18] when compared with pure organic polymers. Additionally, the properties of the composite materials depend upon the morphology of the phases, *viz.* organic and/or inorganic network, which has to be controlled over several length scales. Therefore, the development of such materials is a 'land of multidisciplinary,'[1] where chemists, physicists, material scientists, and engineers have to work closely together to fully exploit this technical opportunity for creating new materials and devices.

One important class of hybrid materials is that in which the inorganic fraction is composed of conducting polymers, in which new inorganic lattice structures are formed, resulting from cooperative interactions between the organic and inorganic components. In all cases, there is possibility of developing new materials with properties not seen in purely organic or purely inorganic solids. In recent past, such materials have shown excellent ion-exchange properties.[19–21] Composite materials consisting of conducting polymers have an additional advantage in making ion-selective membrane electrodes.[22,23]

Kinetic studies are helpful in understanding the ion-exchange mechanism undergoing in a particular system on the basis of rate of exchange[24–28] using Nernst–Plank equation[29–31] with some additional assumptions. In the present research work, kinetic study of some divalent metal ions on polypyrrole Th(IV) phosphate has been performed to understand its ion-exchange mechanism. As a result, some useful physical parameters such as self-diffusion coefficient (D_0), energy of activation (E_a), and entropy of activation (ΔS^*) have been determined. Electrical conductivity properties have also been studied in the present work.

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EXPERIMENTAL

Reagents and instruments

The reagents used for the synthesis of material were obtained from CDH, E- Merck and Qualigens (India). All other reagents and chemicals were of analytical reagent grade. A four-in-line probe dc electrical conductivity-measuring instrument, Scientific Equipment (India), was used for measuring dc electrical conductivity. A hydraulic pressure instrument was used for making pellets of sample materials. A water bath incubator shaker having a temperature variation of ±0.5°C was used for all equilibrium studies.

Preparation of polypyrrole Th(IV) phosphate

The 'organic-inorganic' electrically conducting composite cation-exchanger was synthesized as reported earlier,[32] in which inorganic precipitate was prepared by mixing a solution of 0.1*M* $Th(NO_3)_4\ 5H_2O$ prepared in 1*M* HNO_3 at the flow rate of 0.5 mL min^{-1} to a solution of 2*M* H_3PO_4 prepared in DMW (demineralized water) at a temperature of 85 ± 5°C. Constant stirring was done during mixing using a magnetic stirrer and a white gel type slurry was obtained. After digestion of the mixture for several hours, it was cooled to room temperature. In the digested slurry of inorganic precipitate of Th(IV) phosphate, 0.1*M* $FeCl_3$ solution prepared in DMW was mixed thoroughly, to which ~ 33.33% (v/v, in toluene) solution of pyrrole was added dropwise and mixed thoroughly, continuous stirring was done during the addition of pyrrole solution. The white inorganic precipitate gel slowly turned first to green and then to black. The reaction mixture was kept for 24 h under ambient condition (25 ± 2°C). Now the polypyrrole based composite gel was filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ferric chloride. The washed gel was then dried over P_4O_{10} at 30°C in an oven. The dried product was immersed in DMW to obtain small granules. These were converted to the H^+- form by placing them in 1*M* HNO_3 for 24 h with occasional shaking intermittently, replacing the supernatant liquid with a fresh acid. The excess acid was removed after several washings with DMW and again the material was dried at 40°C and sieved to obtain particles of particular size range (~ 125 μm). The sample (S-1) prepared with ~ 33.33% pyrrole solution showed high stability and maximum ion-exchange capacity (1.56 meq dry/g for Na^+), was chosen for detailed studies of electrical conductivity and ion exchange kinetics. Conditions of preparation and the ion-exchange capacity of polypyrrole Th(IV) phosphate composite cation-exchange material (sample S-1) are given below:

	Mixing volume ration (v/v)						
Sample	0.1 M $Th(NO_3)_4 \cdot 5H_2O$ in 1 M HNO_3	2 M H_3PO_4	Digestion time (h)	0.1 M $FeCl_3$	Pyrrole in toluence (33.33%)	Appearance of the beads after drying	Na^+ Ion-exchange capacity (meq $dryg^{-1}$)
S-1	5	2	5	2	0.30	Blackish granular	1.56

Electrical conductivity measurements

The composite samples were treated with 0.5*M* aqueous solution of HCl and washed repeatedly with DMW to remove excess HCl until the filtrates gave a negative test for hydrogen ions. The sample materials were dried completely at 50°C in the oven. Then ~ 0.5 g material from each sample was finely grounded in a mortar pastel and pellets were made at room temperature with the help of a hydraulic pressure instrument at 25 kN pressure for 20 min. The thickness of each pellet was measured by a micrometer.

Four-probe electrical conductivity measurements with increasing temperatures (between 35 and 200°C) for the composite cation-exchanger 'polypyrrole:Th(IV) phosphate' samples were performed on pressed pellets by using a 4-in-line-probe dc electrical conductivity-measuring technique. The sample to be tested was placed on the base plate of the four-probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure was applied on the probes and then it was tightened in this position so as to avoid piercing the samples by the probes. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply was then switched on, the temperature was allowed to increase gradually, and the current and voltage were recorded with rise in temperature.

The current-voltage data so generated by a 4-in-line probe dc electrical conductivity measuring instrument was processed for calculation of resistivity (ρ_o), using the following equation:

$$\rho_o = (V/I) \times 2\pi S \quad (1)$$

where V is the voltage (V) and I is the current (A).

Because the thickness of the sample is small when compared with the probe distance and so a correc-

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tion factor has to be applied for it and the corrected resistively may be calculated as:

$$\rho = \rho_o/G_7(W/S) \quad (2)$$

where ρ is the corrected resistively in Ω cm, $G_7(W/S)$ is the correction factor used in the case of nonconducting bottom surface and it is a function of W, thickness of the sample under test (cm) and S, probe spacing (cm); i.e.,

$$G_7(W/S) = (2S/W)\log_e 2 \quad (3)$$

Thus, the electrical conductivity (σ) was calculated using the following equation:

$$\sigma = 1/\rho \quad (4)$$

where σ is the electrical conductivity in S cm^{-1}.

This composite material was also treated with 0.5*M* NaCl, KCl, LiCl, $CaCl_2$, $Pb(NO_3)_2$, $MnCl_2$, and $Cu(NO_3)_2$ solutions, and electrical conductivity measurements were carried out on different forms (Na^+, K^+, Li^+, Ca^{2+}, Pb^{2+}, Mn^{2+}, and Cu^{2+}) of composite cation-exchanger.

The isothermal stability of polypyrrole Th(IV) phosphate composite in terms of dc electrical conductivity retention was carried out on the selected samples (treated with 0.5*M* HCl) at 50, 70, 90, 110, and 130°C in an air oven. The electrical conductivity measurements were carried out at an interval of 15 min. The thermal stability of the composite material in terms of dc electrical conductivity retention was also studied by a cyclic measurement of the dc electrical conductivity on pressed pallets with increasing temperature from 30 to 200°C. The measurements were repeated on the same sample in this temperature range for five times at intervals of 45 min.

Kinetic measurements

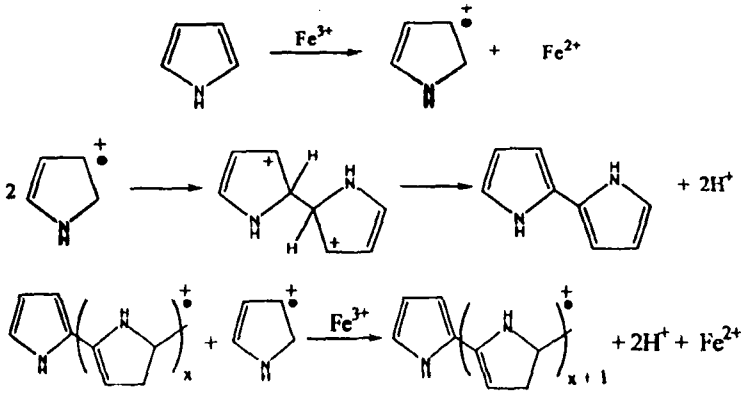
The composite cation-exchange material was treated with 0.5*M* HNO_3 for 24 h at room temperature with occasional shaking; intermittently replacing the supernatant liquid with a fresh acid to ensure the complete conversion to H^+-form and the excess acid was removed after several washing with DMW. Now the dried ion-exchanger sample in the H^+-form was grounded and then sieved to obtain particles of definite mesh sizes (25–50, 50–70, 70–100, and 100–125 μm). Out of them, the particles of mean radii ~ 125 μm (50–70 mesh) were used to evaluate various kinetic parameters. The rate of exchange was determined by limited bath technique as follows:

Twenty milliliter fractions of the 0.02*M* metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn, and Zn) were shaken with 200 mg of the cation-exchanger in H^+-form in several stoppered conical flasks at desired temperatures [25, 33, 50, and 65 (± 0.5)°C] for different time intervals (0.5, 1.0, 2.0, 3.0, and 4.0 min). The supernatant liquid was removed immediately and determinations were made usually by EDTA titrations.[33] Each set was repeated four times and the mean values were taken for calculations.

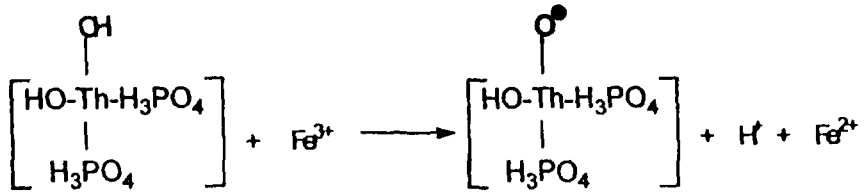
RESULTS AND DISCUSSION

Preparation and electrical conductivity measurement studies of polypyrrole Th(IV) phosphate

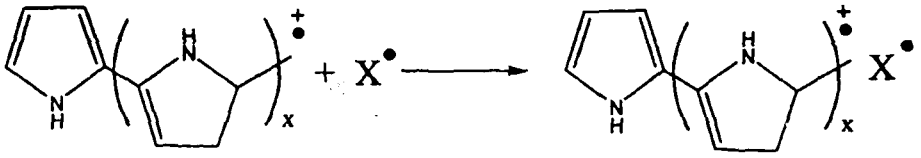
For this study, sample of polypyrrole Th(IV) phosphate, an electrically conducting composite cation-exchanger was chemically prepared by incorporation of polypyrrole, a conducting polymer into inorganic matrices of fibrous type Th(IV) phosphate. The sample prepared with ~ 33.33% pyrrole solution showed high chemical, mechanical, and thermal stability[32] and maximum ion-exchange capacity (1.56 meq dry/g for Na^+),[32] was selected for detailed studies of electrical conductivity and ion-exchange kinetics. The polymerization reaction for the synthesis of polypyrrole is a very complicated one. The initial oxidation step, in which a radical cation is formed is followed by a coupling reaction, deprotonation, and one-electron oxidation to regenerate the aromatic system,[34] using $FeCl_3$ in aqueous medium at room temperature (25 ± 2°C) as given in the following reactions:



When aqueous solution of $FeCl_3$ was added with the inorganic precipitate of thorium(IV) phosphate, Fe^{3+} may convert thorium phosphate into a radical that can be shown as:



Hence, the binding of polypyrrole into the matrix of thorium(IV) phosphate can be shown as:



Polypyrrole — Thorium(IV) phosphate matrix — Polypyrrole Th(IV) phosphate

This composite material contains two components, *viz.* inorganic and organic. The inorganic component is an efficient ion-exchange material whereas organic component, polypyrrole, is a good electrically conducting polymer. The dc electrical conductivity of composite is because of the presence of sufficient amount of the conducting polymer and basically, it is electronic conduction contributed by the conducting component, i.e., polypyrrole by the charge-transfer reaction between polypyrrole component of the composites and doping agents, HCl.

$$[\text{Polypyrrole Th(IV) phosphate}] + n\ \text{HCl} \rightarrow [\text{Polypyrrole } (n\text{H})(\text{Th(IV) phosphate})]^{+n}(n\ \text{Cl}^-) \quad (5)$$

Controlling the doping process, the electrical conductivity of these materials could be varied from insulator, through semiconductor to metal range. A redox reaction for ammonia and amine intercalation into layered chalcogenides has been reported by Schöllhörn and Zagefka[35] and further supported by the work of Foot and Shaker.[35] Thus, the neutralization reactions to undope polypyrrole within polypyrrole Th(IV) phosphate composite cation-exchange material by ammonia may be suggested as given below:

$$[\text{Polypyrrole } (n\text{H})\ (\text{Th(IV)phosphate})]^{+n}(n\ \text{Cl}^-) + n\ \text{NH}_4^+ + n\ \text{e}^- \rightarrow [\text{Polypyrrole Th(IV) phosphate}] + n\ \text{NH}_4\text{Cl} \quad (6)$$

In the present study, the variations of electrical conductivity (σ) of the polypyrrole Th(IV) phosphate composite samples (as prepared and doped with HCl and prepared with 33.33% pyrrole concentration, vol %) by raising temperatures (between 30 and 140°C) are carried out. On examination, it was observed that the electrical conductivity of the samples increase with the increase in temperature and the values lie in the order of 10^{-6} to 10^{-4} S cm^{-1}, i.e., in the semiconductor region. To determine the nature of dependence of electrical conductivity on temperature, plots of log σ versus 10^3 T^{-1} (K^{-1}) were drawn (Fig. 1) and they followed Arrhenius equation similar to other semiconductors.[37] F1

The dependence of the electrical conductivity through the bi-phasic systems (polypyrrole Th(IV) phosphate composites; prepared with different concentrations of pyrrole monomer) on the concentration of conducting phase, i.e., polypyrrole was also examined (Table I). A slight increase in electrical conductivity for the composite is followed at a certain pyrrole concentration by a sudden jump, which is again followed by moderate T1

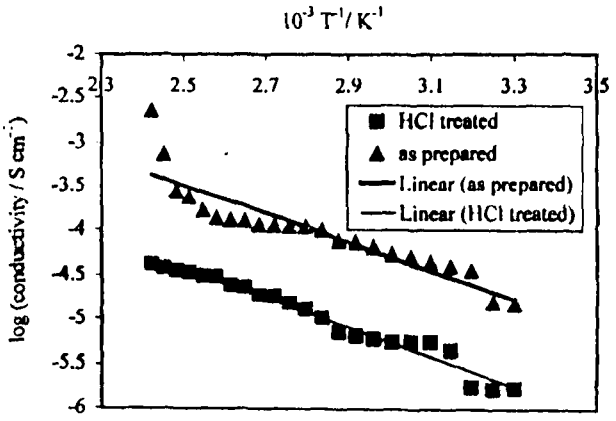


Figure 1 Arrhenius plots for polypyrrole Th(IV) phosphate composite material.

TABLE I
Values of dc Electrical Conductivity for the Polypyrrole and Polypyrrole Th(IV) Phosphate Composites with Different Concentrations of Pyrrole Monomer

Sample No.	Polypyrrole (prepared with 33.33% pyrrole in toluene) Ambient temperature dc electrical conductivity (S cm^{-1})	Polypyrrole Th(IV) phosphate Pyrrole monomer concentration (vol %)	Polypyrrole Th(IV) phosphate Ambient temperature dc electrical conductivity (S cm^{-1})
1	3.28×10^{-5}	3.33	4.13×10^{-8}
2	–	6.66	5.19×10^{-8}
3	–	10	2.82×10^{-8}
4	–	13.33	3.84×10^{-8}
5	–	16.66	5.92×10^{-8}
6	–	20	6.15×10^{-8}
7	–	23.33	2.53×10^{-5}
8	–	26.66	3.47×10^{-5}
9	–	30	3.54×10^{-5}
10	–	33.33	3.82×10^{-4}
11	–	36.66	4.90×10^{-4}
12	–	40	5.16×10^{-4}

increase (Table I). At about 23.33% pyrrole concentration (critical concentration of conducting phase), this sharp rise in electrical conductivity is observed, which could possibly be explained on the basis of percolation theory.[38] It was also observed that the ambient temperature conductivities of the composite for some concentrations of pyrrole monomers are greater than that of polypyrrole as shown in Table I. The effect on electrical conductivity of the different forms (Na^+, K^+, Li^+, Ca^{2+}, Pb^{2+}, Mn^{2+}, and Cu^{2+}), of composite cation-exchanger
T2 was also examined (Table II). It was observed that the electrical conductivity was affected negligibly when treated with the metal nitrate solutions of (Na^+, K^+, Li^+, and Ca^{2+}), while the electrical conductivity of Pb^{2+}, Cu^{2+}, and Mn^{2+} forms were decreased to 10^{-8} S cm^{-1} beyond the semiconducting region (Table II).

The thermal stability of the composite material (HCl treated) in terms of dc electrical conductivity retention was studied under isothermal condition (at 50, 70, 90, 110, 130, and 150°C) by measuring four-probe-in-line dc electrical conductivity at an interval of 15 min. The electrical conductivity measured with respect to the time of accelerated ageing is presented in Figure 2. It F2 was observed that the electrical conductivity for polypyrrole Th(IV) phosphate composite material is quite stable at 50, 70, 90, and 110°C that supports the fact that the dc electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150°C that may be attributed to the loss of dopant and the chemical reaction of dopant with the material.

The stability of the material (HCl treated) in terms of electrical conductivity retention was also monitored for five cycles by repeatedly measuring linear four-probe dc electrical conductivity with increase in temperature at an interval of 1 h and the dc conductivity for each heating cycle was plotted as log σ versus 10^3 T^{-1} (K^{-1}) as shown in Figure 3. It was observed that F3

TABLE II
Four-Probe dc Electrical Conductivity of Different Forms of Polypyrrole Th(IV) Phosphate Composite System at Ambient Temperature (Prepared with 33.33% Pyrrole Monomers)

Sample No.	Polypyrrole Th(IV) phosphate composite	Conductivity (S cm^{-1})
1	As prepared	1.68×10^{-6}
2	HCl treated	1.46×10^{-4}
3	NaCl treated	2.27×10^{-5}
4	KCl treated	1.25×10^{-5}
5	LiCl treated	1.84×10^{-5}
6	$CaCl_2$ treated	1.74×10^{-5}
7	$Pb(NO_3)_2$ treated	2.04×10^{-8}
8	$MnCl_2$ treated	1.26×10^{-8}
9	$Cu(NO_3)_2$ treated	2.02×10^{-8}

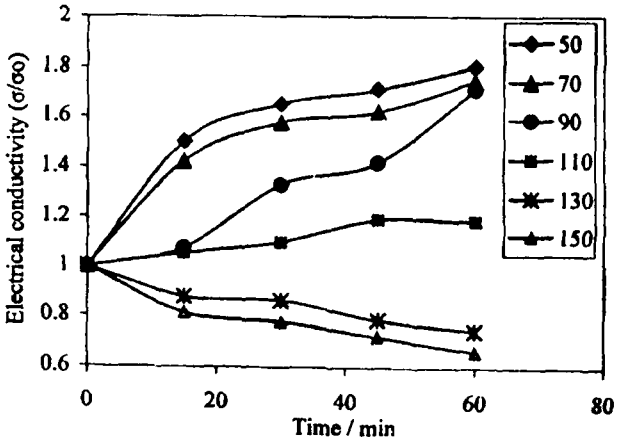


Figure 2 Isothermal stability of polypyrrole Th(IV) phosphate composite (HCl treated) in terms of retention of dc electrical conductivity with respect to time at 50, 70, 90, 110, 130, and 150°C.

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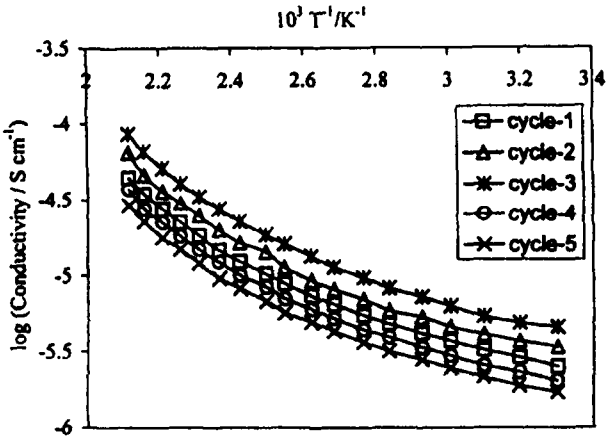

Figure 3 Arrhenius plots of retention of dc electrical conductivity for polypyrrole Th(IV) phosphate composite (HCl treated) during heating-cooling cycles up to 200°C.

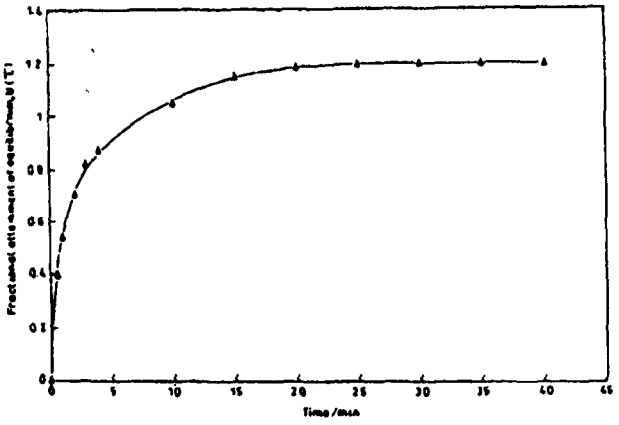

Figure 5 A plot of $U(\tau)$ versus t (time) for M(II)-H(I) exchanges at 33°C on polypyrrole Th(IV) phosphate composite cation-exchanger for the determination of infinite time.

each plot followed the Arrhenius equation for its temperature dependence similar to other semiconductors.[37] There was minor difference in their electrical conductivity even after repeating the experiment for five times which showed the good stability of the material during heating-cooling cycles under severe oxidizing conditions upto 200°C. This composite material was also observed to be a stable material, i.e., the room temperature conductivity is negligibly affected by short-term exposure to laboratory air as evident from Figure 4.

Ion-exchange kinetics of polypyrrole Th(IV) phosphate composite cation-exchanger

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Mg(II)-H(I), Ca(II)-H(I), Sr(II)-H(I), Ba(II)-H(I), Ni(II)-H(I), Cu(II)-H(I), Mn(II)-H(I), and Zn(II)-H(I). The particle diffusion-controlled phenomenon is favored by a high metal ion concentration, a relatively large particle size of the exchanger, and vigorous shaking of the exchanging mixture.

The infinite time of exchange is the time necessary to obtain equilibrium in an ion exchange process. The ion-exchange rate becomes independent of time after this interval. Figure 5 shows that 20 min were required for the establishment of equilibrium at 33°C for Mg^{2+}-H^+ exchange. Similar behavior was observed for Ca^{2+}-H^+, Sr^{2+}-H^+, Ba^{2+}-H^+, Ni^{2+}-H^+, Cu^{2+}-H^+, Mn^{2+}-H^+, and Zn^{2+}-H^+ exchanges. Therefore, 20 min was assumed to be the infinite time of exchange for the system. A study of the concentration effect on the rate of exchange at 33°C showed that the initial rate of exchange was proportional to the metal ion concentration at and above 0.02M (Fig. 6). Below 0.02M concentration, film diffusion control was more prominent.

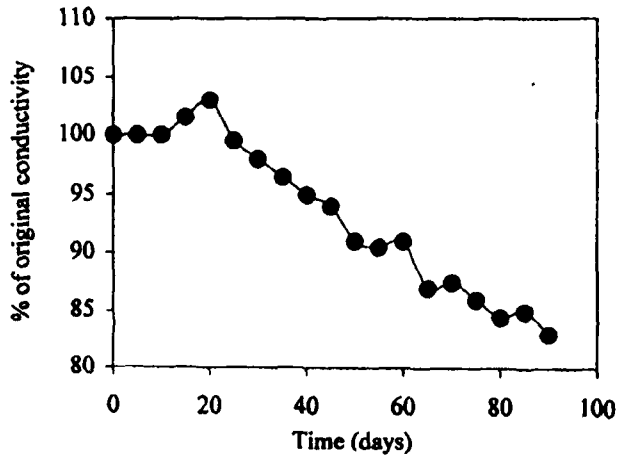

Figure 4 Conductivity versus time of exposure to laboratory air for polypyrrole Th(IV) phosphate composite material (HCl) treated.

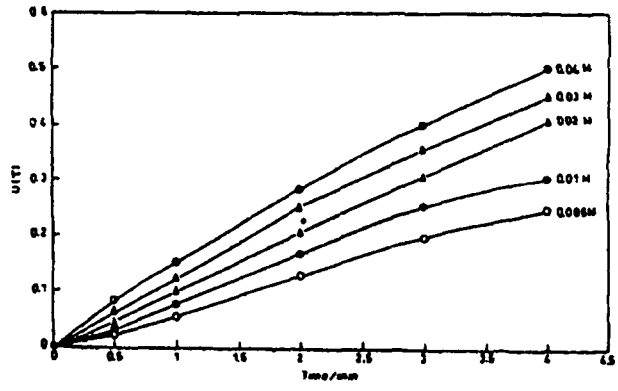

Figure 6 Plots of $U(\tau)$ versus t (time) for M(II)-H(I) exchanges using different metal solution concentrations at 33°C on polypyrrole Th(IV) phosphate composite cation-exchanger.

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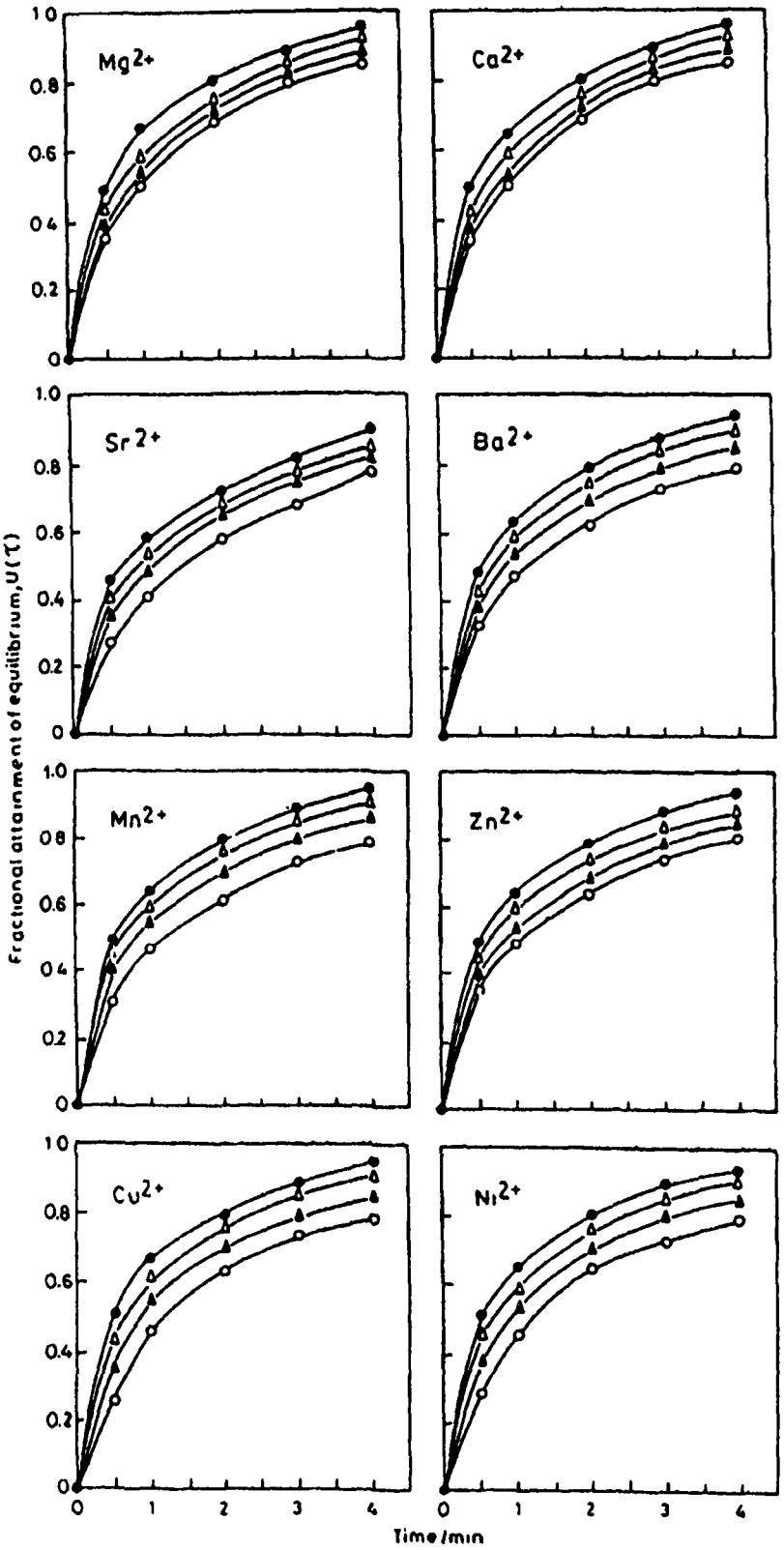

Figure 7 Plots of $U(\tau)$ versus t (time) for different M(II) H(I) exchanges at different temperatures on polypyrrole Th(IV) phosphate composite cation-exchanger: (□) 25 C, (▲) 33 C, (Δ) 50 C, and (●) 65 C.

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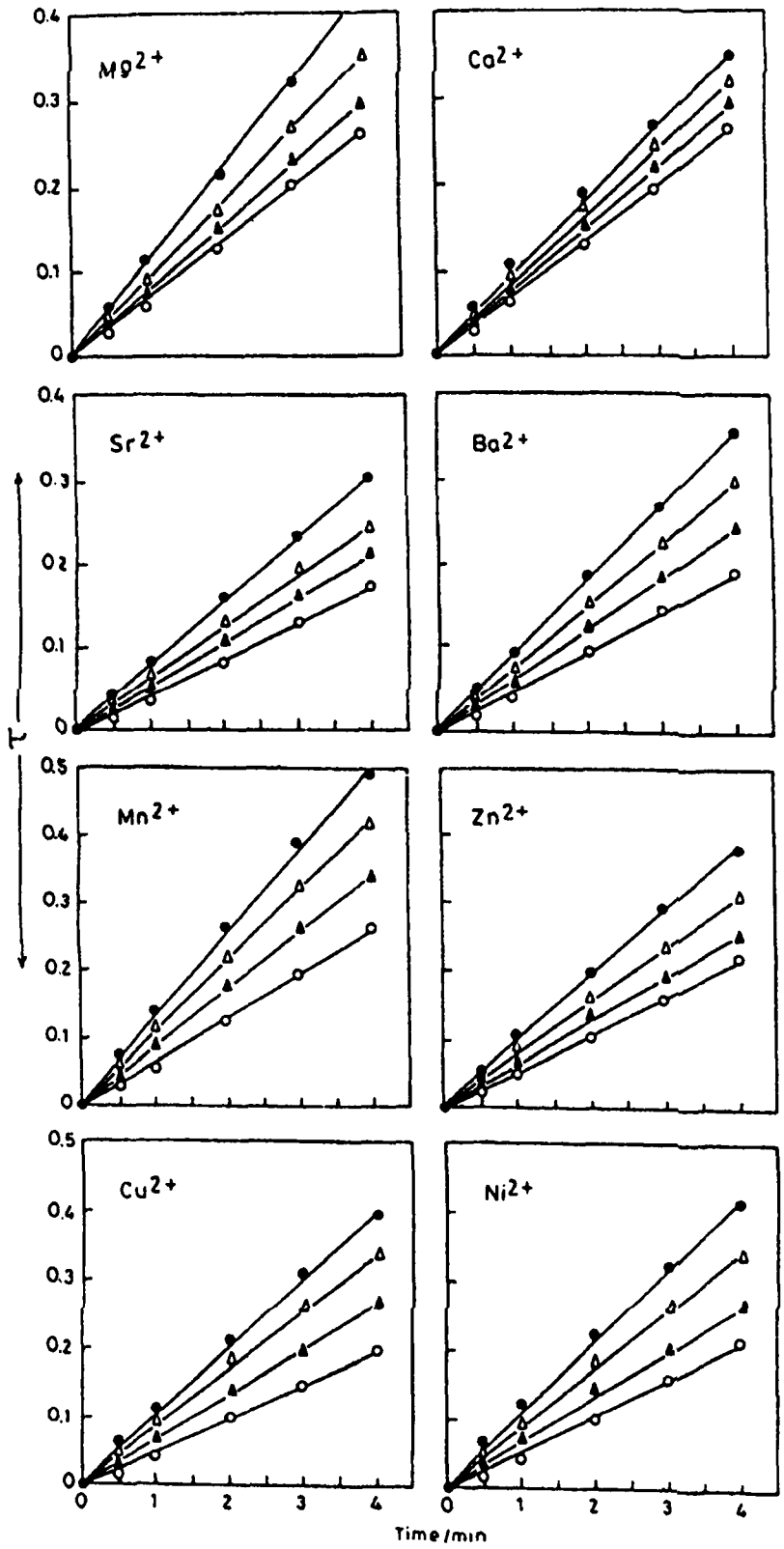

Figure 8 Plots of τ versus *t* (time) for different M(II)-H(I) exchanges at different temperatures on polypyrrole Th(IV) phosphate composite cation-exchanger: (□) 25°C, (▲) 33°C, (Λ) 50°C, and (●) 65°C.

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TABLE III
Slopes of Various τ Versus Time (*t*) Plots on Polypyrrole Th(IV) Phosphate Cation-Exchanger at Different Temperatures

Migrating ions	Slope (10^2 s^{-1})			
	25°C	33°C	50°C	65°C
Mg(II)	6.48	7.38	8.73	10.61
Ca(II)	6.48	7.27	8.06	8.88
Sr(II)	4.21	5.24	6.19	7.62
Ba(II)	4.70	6.08	7.45	8.93
Cu(II)	4.85	6.59	8.46	10.10
Ni(II)	5.23	6.68	8.58	10.62
Zn(II)	5.36	6.41	7.74	9.68
Mn(II)	6.35	8.53	10.52	12.73

The results are expressed in terms of the fractional attainment of equilibrium, $U(\tau)$ with time according to the equation:

$$U(\tau) = \frac{\text{The amount of exchange at time } "t"}{\text{The amount of exchange at infinite time}} \quad (7)$$

Plots of $U(\tau)$ versus time (t) (min), for all metal ions (Fig. 7) indicated that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with an increase in temperature and the uptake decreased with time. Each value of $U(\tau)$ will have a corresponding value of τ, a dimensionless time parameter. On the basis of the Nernst–Planck equation, the numerical results can be expressed by explicit approximation[39–41]:

$$U(\tau) = \{1 - \exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2} \quad (8)$$

where τ is the half-time of exchange $= \overline{D}_{H^+} t/r_0^2$, α is the mobility ratio $= \overline{D}_{H^+}/\overline{D}_{M^{2+}}$, r_0 is the particle radius, $\overline{D}_{H^+}$ and $\overline{D}_{M^{2+}}$ are the inter diffusion coefficients of counter ions H^+ and M^{2+} in the exchanger phase, respectively. The three functions $f_1(\alpha)$, $f_2(\alpha)$, and $f_3(\alpha)$ depend upon the mobility ratio (α) and the charge ratio ($Z_{H^+}/Z_{M^{2+}}$) of the exchanging ions. Thus, they have different expressions as given below. When the exchanger is taken in the H^+-form and the exchanging ion is M^{2+}, for $1 \leq \alpha \leq 20$, as in the present case, the three functions have the values:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\,\alpha^{0.668}}$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\,\alpha^{0.4635}}$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\,\alpha^{1.140}}$$

The value of τ was obtained on solving eq. (10) using a computer. The plots of τ versus time (t) at the four temperatures, as shown in Figure 8, are straight lines passing through the origin, confirming the particle diffusion control phenomenon for M(II)–H(I) exchanges at a metal ion concentration of 0.02*M*.

The slopes (S values) of various τ versus time (t) plots are given in Table III. The S values are related to $\overline{D}_{H^+}$ as follows:

$$S = \overline{D}_{H^+}/r_0^2 \quad (9)$$

The values of $-\log \overline{D}_{H^+}$ obtained by using eq. (9) plotted against $1/T$ are straight lines as shown in Figure 9, thus verifying the validity of the Arrhenius relation:

$$\overline{D}_{H^+} = D_0 \exp(-E_a/RT) \quad (10)$$

D_0 is obtained by extrapolating these lines and using the intercepts at the origin. The activation energy (E_a) is then calculated with the help of the eq. (10), by substituting the value of $\overline{D}_{H^+}$ at 273 K. The entropy of activation (ΔS^*) was then calculated by substituting D_0 in eq. (11).

$$D_0 = 2.72d^2\,(kT/h)\exp(\Delta S^*/R) \quad (11)$$

where d is the ionic jump distance taken as 5×10^{-10} m,[26] k is the Boltzmann constant, R is the gas constant, h is Plank's constant and T is taken as 273 K. The values of the diffusion coefficient (D_0), energy of activation (E_a), and entropy of activation (ΔS^*), thus obtained are summarized in Table IV.

The kinetic study reveals that equilibrium is attained faster at a higher temperature (Fig. 6), probably because of a higher diffusion rate of ions through the thermally enlarged interstitial positions of the ion-exchange matrix. The particle diffusion phenomenon is evident from the straight lines passing through the origin for the τ versus time (t) plots, as shown in Figure 8. The values of activation energy indicate the

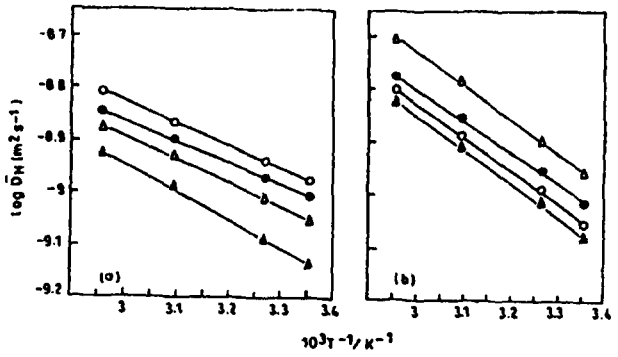

Figure 9 Plots of $-\log D_H$ vs 10^3 T^{-1} (K^{-1}) for: (a) (□) Mg (II), (●) Ca(II), (Δ) Ba(II), (▲) Sr(II), and (b) (Δ) Mn(II), (●)Ni(II), (□) Cu(II), (▲) Zn(II), on polypyrrole Th(IV) phosphate composite cation-exchanger.

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TABLE IV
Values of D_0, E_a, and ΔS^* for the Exchange of H(I) with Some Metal Ions on Polypyrrole Th(IV) Phosphate Composite Cation-Exchange Material

Metal ion exchange with H(I)	Ionic mobility (10^9 m^2 V^{-1} s^{-1})	Ionic radii (10^2 nm)	D_0 (10^8 m^2 s^{-1})	E_a (10^2 kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
Mg(II)	55	7.8	2.86	42.71	−1.21
Ca(II)	62	10.6	2.39	41.29	−1.29
Sr(II)	62	12.7	4.61	53.85	−1.00
Ba(II)	66	14.3	2.83	44.80	−1.22
Cu(II)	57	7.0	11.34	62.70	−0.61
Ni(II)	52	7.8	9.80	59.67	−0.68
Zn(II)	56	8.3	12.00	64.16	−0.59
Mn(II)	55	9.1	16.26	64.56	−0.46

minimum energy required for [M(II)–H(I)] ion-exchange process. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange [M(II)–H(I)] process.

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Electrical conductivity and ion-exchange kinetic studies of a crystalline type 'organic–inorganic' cation-exchange material: polypyrrole/polyantimonic acid composite system, $(Sb_2O_5)\ (-C_4H_2NH-)\cdot nH_2O$

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Abstract

An electrically conducting 'organic–inorganic' crystalline type composite cation-exchange material, the polypyrrole/polyantimonic acid system was prepared by incorporating polypyrrole into an inorganic precipitate of polyantimonic acid. The temperature dependence of the electrical conductivity of this composite system was measured on compressed pellets by using a 4-in-line-probe dc electrical conductivity-measuring instrument. The conductivity values lie in the semiconductor region, i.e., they are of the order of 10^{-5}–10^{-4} S cm^{-1} and follow the Arrhenius equation. The energy of activation of electrical conduction was also calculated. This system also possessed an improved ion-exchange capacity, high chemical and thermal stabilities, reproducibility and selectivity for some specific metal ions. Kinetic studies of exchange for some divalent metal ions of alkaline earths and transition metals were carried out under conditions favoring a particle diffusion-controlled ion-exchange phenomenon and some physical parameters such as the self diffusion coefficient D_0, the energy of activation E_a and the entropy of activation ΔS^* were determined.

Keywords: Organic–inorganic composite material; Cation-exchanger; Electrical conductivity; Ion-exchange kinetics; Polypyrrole/polyantimonic acid system; Semiconductor

1. Introduction

Inorganic ion-exchange materials based on polyvalent metals have been established to have applications in various disciplines, i.e., metal ion separation, preconcentration, catalysis, environmental studies, medical science (kidney dialysis), ion-selective electrode preparation, heterogeneous solid state membrane formation and in ion-exchange fibers preparation, etc. Besides their other advantages, these materials are important in being more stable to high temperatures and radiation fields than organic ion-exchange materials. Systematic studies on the adsorption behavior of the hydroxides and hydrous oxides of multivalent metals indicated that 'so-called' crystalline antimonic acid behaved as an excellent cation-exchange material [1,2]. The formation of polyantimonic acid was carried out by adjusting the pH of a highly acidic potassium pyroantimonate solution [3]. Since it was known that, in slightly acidic solution, antimony salts are polymerized, the inorganic precipitate was termed 'polyantimonic acid' [4]. It appears that the starting material used for the preparation of the inorganic antimonic acid or antimonates plays an important role in determining its properties. The antimonic acid prepared by taking potassium pyroantimonate, $KSb(OH)_6$ [4] as the starting material showed a higher ion-exchange capacity as against $SbCl_5$ [5]. The –OH groups of $KSb(OH)_6$ may have been incorporated into

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the structure of the ion-exchanger, thus increasing the number of replaceable H^+-ions in the exchange sites [6].

Organic polymers as ion-exchangers are well known for their uniformity, chemical stability and control of their ion-exchange properties through synthetic methods [7]. In order to obtain a combination of these advantages associated with polymeric and inorganic materials as ion-exchangers, attempts have been made to develop a new class of composite ion-exchangers by incorporation of electrically conducting organic polymers (polyaniline, polypyrrole, polythiophene, etc.) into the matrices of inorganic precipitates of multivalent metal acid salts. These materials are attractive for the purpose of creating high performance or highly functional polymeric materials that are expected to provide many possibilities; these are termed 'organic–inorganic' hybrid materials. A few such excellent ion-exchange materials have been developed in our laboratory and have been used successfully as ion-selective membrane electrodes and in chromatographic techniques [8–11].

The electrical and electronic properties exhibited by solid-state ionic materials are crucial in a large number of inorganic as well as organo-inorganic materials applications [12–16]. These unique electronic properties result from their extended structures, where strong interactions between the atoms, ions or molecules occur throughout the lattice. In terms of conductivity, the behavior ranges from insulating through semiconducting to metallic and superconducting. Many types of electrically conducting materials classified as electrolytes or polymer ionics have been developed and characterized in recent years [17]. Solid electrolytes, having conductivities of 10^{-1}–10^{-2} S cm^{-1}, are required in several systems operating either with high current densities (electrolyzers, batteries, etc.), or at very low current levels (gauges, electrochemical memories, coulometers, etc.), in order to avoid excessive Joule-heat losses or excessive cell impedance. Furthermore, high conductivities are required for materials employed in the preparation of charged membranes or in thermoelectric generators [18]. Only a few solid electrolytes are presently known to exhibit such a favorable conductance and most of them only at high temperature.

In the past few years, researchers have shown much interest, from both the solid-state scientific and inorganic chemical perspectives, in the study of the electrically conducting behavior of 'organo-inorganic' composite materials [19–24]. Special interest today is focused on composite systems having high conductivity at ambient and sub-ambient temperatures, since they find unique applications, such as for separators in high power, versatile and rechargeable lithium batteries. Moreover, composite materials composed of oxides or polyvalent metal acid salts and conducting polymers have applications in more fields of applications, such as smart windows, toners in photocopying, conductive paints, drug delivery, rechargeable batteries, etc. [25–27]. These novel materials have also generated a large amount of interest in the field of synthetic metals.

Conducting polymers possess good tunable electrical conductivity and are organic electrochromic materials with chemically active surfaces [28,29]. However, they are chemically sensitive and have poor mechanical properties and thus pose a processibility problem. On the other hand, inorganic oxides or metal acid salts show the presence of more sites for surface reactivity and are highly porous in sol form. They also have good mechanical properties and are good dispersants too [30]. Thus composite materials formed by combining conducting polymers and inorganic particles possess all the good properties of both the constituents and therefore an enhanced utility. The properties of such kinds of composites are strongly dependent on the concentration of polymer. Polypyrrole, one of the conducting polymers, has received much attention in the preparation of composites due to its high stability in the conducting oxidized form [31–33]. Beleze and Zarbin [33] have successfully synthesized the organic–inorganic conducting polymer polyantimonic acid composite material. In this paper, we report the preparation of composites of conducting polymer (polypyrrole) and polyvalent metal acid salts (polyantimonic acid) by a process of simultaneous gelation of inorganic acid salts as well as polymerization of the pyrrole monomer by taking different amounts of monomer in fixed volumes of inorganic precipitates. The electrical conductivity behavior of the polypyrrole/polyantimonic acid composite system with increasing temperatures was measured by using a 4-in-line-probe dc electrical conductivity measuring method.

To understand the ion-exchange process, investigations of some kinetic parameters such as the diffusion coefficient, energy and entropy of activation, etc., are very much essential. It is noteworthy that these parameters tell us about the mechanism, rate determining step and rate laws obeyed by the ion-exchange process. These studies enable us to understand the viability of an ion-exchanger in separations of metal ions. Most of the earlier studies [34–37] of kinetic behavior were based on the old *Bt* criterion [38,39], which is not very useful for a true ion-exchange (non-isotopic exchange) process because of the different effective diffusion coefficients and different mobilities [40] of the exchanging ions involved. The Nernst [41] and Planck [42] equations with some additional assumptions provide more appropriate values in obtaining the values of the various kinetic parameters precisely [19,43–48]. Since polypyrrole/polyantimonic acid composite showed promising ion-exchange behavior [3], we have also conducted a kinetic study on the exchange of some divalent metal ions on this material that is useful to understand the mechanism of ion-exchange on the surface of the material and its separation potential. The following pages summarize the results of

our studies on electrical conducting behavior and ion-exchange kinetics for the exchange of some divalent metal ions of this composite material.

2. Experimental

2.1. Reagents and instruments

The reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E- Merck and Qualigens (India Ltd.). All other reagents and chemicals were of analytical reagent grade. An electron microscope (LEO 435 VP, Australia) with an attached imaging device was used for scanning electron microscopy (SEM) and a PW 1710-based diffractometer (Phillips, Holland) was used for XRD (X-ray diffraction) studies. The Fourier transform infrared (FT-IR) spectra were recorded by a Spectrum-BX (Perkin–Elmer, USA) FT-IR spectrophotometer. A four-in-line probe electrical conductivity-measuring instrument, Scientific Equipment (India), was used for measuring the dc electrical conductivity. A hydraulic pressure instrument was used for making pellets of sample materials. An electronic balance (digital), Sartorius (Japan), model 21 OS was used for weighing purpose. A water bath incubator shaker having a temperature variation of ±0.5 °C was used for all equilibrium studies.

2.2. Preparation of polypyrrole/polyantimonic acid composite cation-exchanger

The polyantimonic acid product was obtained by dissolving 0.05 mol of potassium pyroantimonate, $KSb(OH)_6$ in 5.8 M HCl. The solution was kept overnight at room temperature (25 ± 2 °C) and thereafter neutralized with concentrated NH_4OH until a residual acidity of 0.75 M HCl was obtained. A white gel was obtained.

A solutions of pyrrole (≈3.33–40%, vol%) in CCl_4 was mixed thoroughly with the fixed volume of inorganic precipitate of polyantimonic acid, to which 0.1 M $FeCl_3$ solution prepared in demineralized water (DMW) was added drop wise. Continuous stirring was done during the addition of ferric chloride solution; slowly the white inorganic precipitate gel turned first to green and then to black. The reaction mixture was then kept for 24 h under ambient conditions (25 ± 2 °C). Then the polypyrrole based composite gel was filtered off, washed with 0.75 M HCl and then washed thoroughly with DMW to remove excess acids and any adhering traces of ferric chloride. After filtration the gel was dried at 50 °C in an air oven for 48 h. The dry product was then crushed into small granules when immersed in DMW. The material was again washed with acetone in a soxhlet, finally dried at 50 °C and kept in a desiccator. Hence a number of composite samples of polypyrrole/polyantimonic acid were prepared with different concentrations (vol%) of pyrrole solutions, but the sample prepared with ≈33.33% pyrrole solution showed high stability and maximum ion-exchange capacity (3.19 meq dry g^{-1} for Na^+), and was chosen for detailed studies of electrical conductivity and ion-exchange kinetics.

2.3. Electrical conductivity measurements

The composite samples were treated with 0.5 M aqueous solution of HCl and washed repeatedly with DMW to remove excess HCl until the filtrates gave a negative test for hydrogen ions. The sample materials were dried completely at 50 °C in the oven. Then ~0.5 g material from each sample was finely ground in a mortar pastel and pellets were made at room temperature with the help of a hydraulic pressure instrument at 25 KN pressure for 20 min. The thickness of each pellet was measured by a micrometer.

Four-probe electrical conductivity measurements with increasing temperatures (between 35 and 200 °C) for the composite samples were performed on pressed pellets by using a 4-in-line-probe dc electrical conductivity-measuring technique. The sample to be tested was placed on the base plate of the four-probe arrangement and the probes were allowed to rest in the middle of the sample. A very gentle pressure was applied on the probes and then it was tightened in this position so as to avoid piercing the samples by the probes. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply was then switched on, the temperature was allowed to increase gradually, and the current and voltage were recorded with rise in temperature.

2.4. Kinetic measurements

The composite cation-exchange material was treated with 0.5 M HNO_3 for 24 h at room temperature with occasional shaking. Intermittently the supernatant liquid was replaced with fresh acid to ensure the complete conversion to the H^+-form and the excess acid was removed after several washings with DMW. Then the dried ion-exchanger sample in the H^+-form was ground and then sieved to obtain particles of definite mesh sizes (25–50, 50–70, 70–100 and 100–125 μm). From these, the particles of mean radii ~125 μm (50–70 mesh) were used to evaluate various kinetic parameters. The rate of exchange was determined by the limited bath technique as follows.

Twenty milliliter fractions of the 0.02 M metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn) were shaken with 200 mg of the cation-exchanger in H^+-form in several stoppered conical flasks at the desired

temperatures [25, 33, 50 and 65 (±0.5) °C] for different time intervals (0.5, 1.0, 2.0, 3.0 and 4.0 min). The supernatant liquid was removed immediately and determinations were made, usually by EDTA titration [49]. Each set was repeated four times and the mean value was taken for calculations.

3. Results and discussion

3.1. Preparation of polypyrrole/polyantimonic acid

In this endeavor, an electrically conducting 'organic–inorganic' composite cation-exchange material, polypyrrole/polyantimonic acid, which possessed a high ion-exchange capacity, reproducible behavior and high stability, was prepared chemically. The material had reasonably good chemical stability, as it was resistant to 2 M $HClO_4$ and 2 M H_2SO_4 and other solvents (DMW, acetone, formic acid, DMS, CH_3COOH, CH_3COONa and $NaNO_3$, etc.). This material was also thermally stable up to 200 °C and it retained about 59% of the initial ion-exchange capacity when heated up to 600 °C.

After dissolving in concentrated HCl, the composite cation-exchange material was analyzed for 'Sb' by a Vis spectrophotometric method [50]. Carbon, hydrogen and nitrogen contents of the material were determined by elemental analysis. The wt% composition of the material was: Sb, 54.46; C, 10.29; H, 2.58; N, 2.92; O, 29.75. Hence, composition studies indicated the molar ratio of Sb, C, H, N and O in the material as 2.15:4.12:12.31:1.0:8.94.

Scanning electron microscopy was performed on the chemically prepared organic polypyrrole at a magnification of ×3500, and the inorganic polyantimonic acid and polypyrrole/polyantimonic acid composite system at a magnification of ×2500. This indicated the binding of inorganic material by the organic polymer as shown in Fig. 1. The X-ray powder diffraction pattern of this material was studied with Cu Kα radiation and clearly exhibited the presence of fourteen sharp peaks, suggesting a crystalline nature of the material (Fig. 2).

The FT-IR studies performed on this material indicated the presence of external water molecules in addition to the –OH groups and the metal oxides present internally in the material (Fig. 3). Frequencies due to the

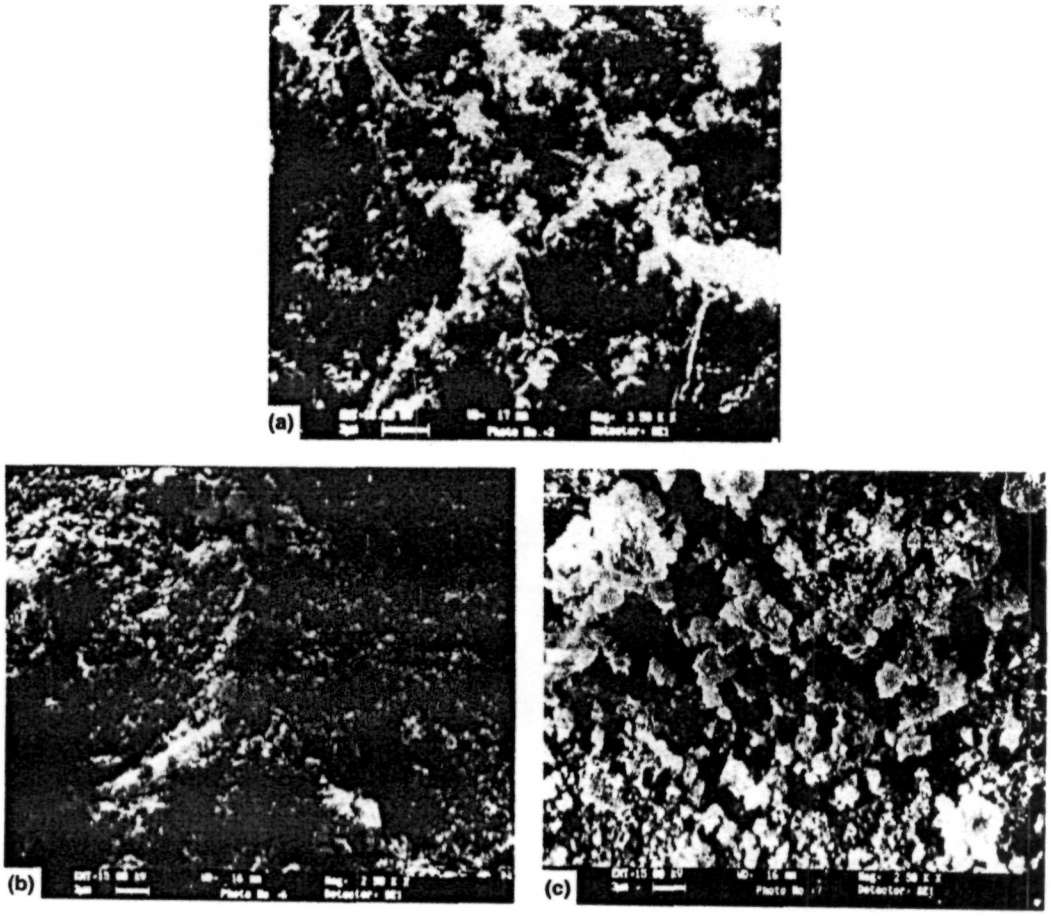

Fig. 1. Scanning electron microphotographs (SEM) of chemically prepared polypyrrole at a magnification ×3500 (a), polyantimonic acid (b) and polypyrrole/polyantimonic acid composite system at a magnification ×2500 (c).

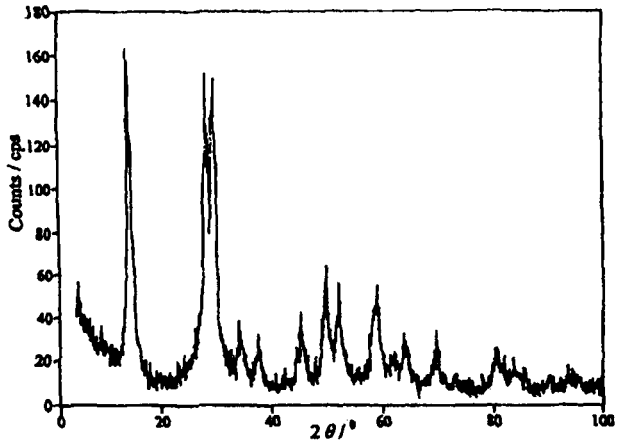

Fig. 2. Powder X-ray diffraction pattern of polypyrrole/polyantimonic acid (as prepared).

Sb–O stretching vibrations [51] have been observed in the region 1100–900 cm^{-1}. The peaks at 1640–1560 cm^{-1} represent the free water molecules (water of crystallization) and are also representative of the strongly bonded –OH groups in the matrix [52]. A sharp peak at around 1400 cm^{-1} can be ascribed to the stretching vibration of C–N [53]. This indicates that the material contains a considerable amount of pyrrole. The FT-IR spectra also confirm the polymerization of pyrrole. The peaks at about 800, 1097 and 3396 cm^{-1} indicate the presence of polypyrrole [54]. The absorption band around 1200 cm^{-1} may be due to C–O stretching [55]. The TGA analysis carried out by an automatic thermal analyzer on heating the material at a constant rate (15 °C min^{-1}) in the air atmosphere showed a continuous loss of mass (about 8.0%) up to 250 °C, which may be due to the removal of the water of crystallization [56]. A further mass loss between 250 and 530 °C may be due to complete decomposition of the organic part of the material. Above 530 °C, a smooth horizontal section is seen, which represents the complete formation of the oxide form of the material as shown in Fig. 4.

On the basis of calculated percentage values for each element and different instrumental analyses (such as FT-IR, TGA-DTA), a tentative formula of the material can be suggested: $[(Sb_2O_5)\ (-C_4H_2NH-)]\cdot nH_2O$. Assuming that only the external water molecules are lost at 250 °C, the ~8.0% loss of mass represented by the TGA curve must be due to the loss of nH_2O from the proposed material. The value of "n", the external water molecules, can be calculated using the equation of Alberti et al. [57]: $18n = X(M + 18n)/100$, where X is the percent mass loss (~7.0%) in the exchanger by heating up to 198 °C, and $(M + 18n)$ is the molar mass

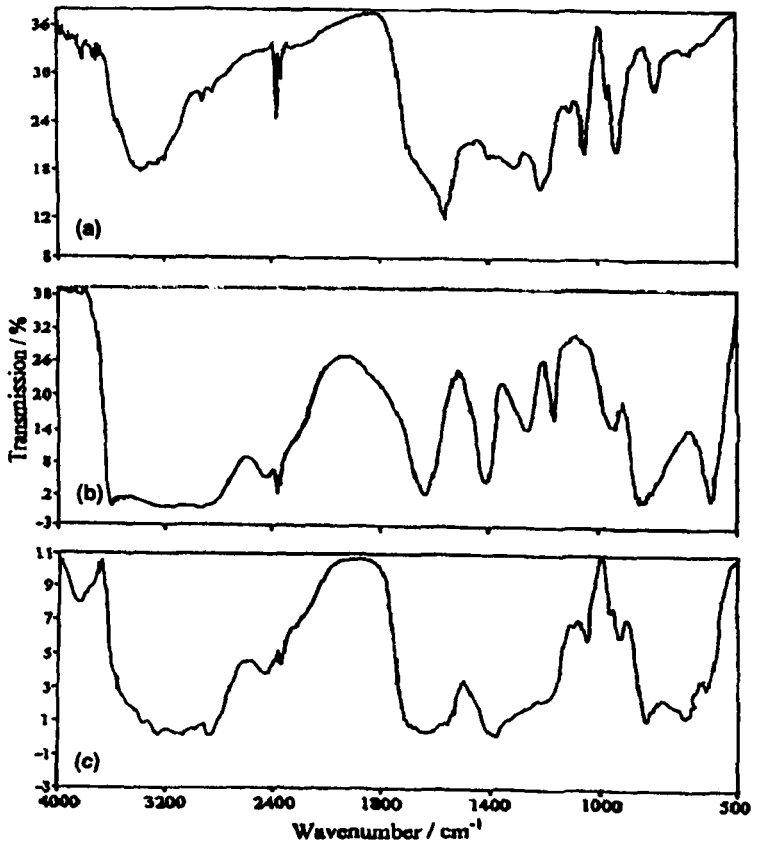

Fig. 3. FT-IR spectra of as prepared polypyrrole (a), polyantimonic acid (b) and polypyrrole/polyantimonic acid composite material (c).

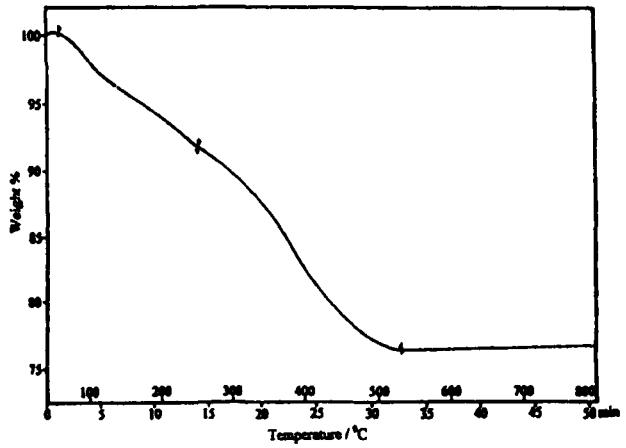

Fig. 4. TGA curve of polypyrrole/polyantimonic acid (as prepared).

of the material. The calculation gives ~2 for the external water molecules (n) per molecule of the composite cation-exchanger.

3.2. Electrical conducting behavior of polypyrrole/polyantimonic acid

Electrical conductivities of the pellets of polypyrrole based polyantimonic acid composite samples were determined from the measurement of conductivity of the samples using the four-probe method of conductivity measurement for semiconductors. This is the most satisfactory method as it overcomes difficulties, which are encountered in conventional methods of conductivity measurement (i.e., two probe), e.g., the rectifying nature of the metal-semiconductor contacts and the injection of minority carriers by one of the current-carrying contacts, which affects the potential of the other contacts and modulates the conductance of the material, etc.

The current–voltage data thus generated at increasing temperatures for the determination of electrical conductivity of the composite sample were processed for calculation of electrical conductivity using the following equation:

$$\sigma = \sigma_0/G_7(W/S), \quad (1)$$

where σ is the electrical conductivity in S/cm, $G_7(W/S)$ is the correction factor used for the case of a non-conducting bottom surface, which is a function of W, the thickness of the sample under test (cm) and S, the probe spacing (cm); i.e.

$$G_7(W/S) = (2S/W)\ln 2 \quad (2)$$

and

$$\sigma_0 = I/(V \times 2\pi S), \quad (3)$$

where I is the current (A) and V is the voltage (V). Although the electrical conductivity measurements were done under ambient conditions, the composite samples were thoroughly dried before making the pellets and performing the electrical conductivity measurements. Hence, the contribution of protonic conductivity to the total electrical conductivity due to the presence of moisture should be minimal and need not be taken into consideration.

The main constituent that makes the composite electrically conductive is polypyrrole when present in sufficient amount. The conducting properties depend on the percolation behavior of the conducting phase. The electrical conductivity of the composite is due to oxidized polypyrrole maintained in its conductive state by polyantimonate counter ions in excess. The dependence of the electrical conductivity through the bi-phasic system (polypyrrole/polyantimonic acid composite; prepared with different concentrations of pyrrole monomer) on the concentration of the conducting phase (polypyrrole) was examined (Table 1). The slight increase in electrical conductivity for the composites was followed at a certain pyrrole concentration by a sudden jump, which was again followed by a moderate increase (Fig. 5). At about 27% pyrrole concentration (critical concentration of conducting phase), this sharp rise in electrical conductivity is observed and could possibly be explained on the basis of percolation theory [58].

The variation of electrical conductivity (σ) of the composite samples (prepared with 33.33 vol% pyrrole concentration, with increasing temperatures (between 35 and 200 °C) was investigated. On examination, it was observed that the electrical conductivities of the samples increase with the increase in temperature and the values are of the order of 10^{-5}–10^{-4} S cm^{-1}, i.e., in the semiconductor region. To determine the nature of the dependence of electrical conductivity on temperature, plots of $\log\sigma$ versus $1000/T$ (T in K) were drawn (Fig. 6) and they followed the Arrhenius equation similarly to other semiconductors [59]. The energies of activation of electrical conduction for the composite samples (as prepared and HCl treated) calculated from the slopes of the Arrhenius plots were 0.055 and 0.062 eV, respectively.

This composite material was also treated with 0.5 M NaCl, KCl, LiCl and $CaCl_2$ solutions, and electrical conductivity measurements were carried out on these different forms (Na^+, K^+, Li^+, Ca^{2+}) of materials. The sample treated with $CaCl_2$ solution showed a higher electrical conductivity at room temperature as given in Table 2.

The thermal stability of the composite material (HCl treated) in terms of dc electrical conductivity retention was studied under isothermal conditions (at 50, 70, 90, 110, 130 and 150 °C) using 4-probe-in-line dc electrical conductivity measurements at 15 min intervals. The electrical conductivity measured with respect to the time of accelerated ageing is presented in Fig. 7. For both the composites, it was observed that the electrical conduc-

Table 1
Values of electrical conductivity at ambient temperature for the polypyrrole/polyantimonic acid composites with different concentrations of pyrrole monomer

	Polypyrrole/polyantimonic acid composites					
[Pyrrole] (%)	23.33	26.67	30	33.33	36.67	40
Electrical conductivity (S cm^{-1})	3.94×10^{-9}	1.83×10^{-5}	4.51×10^{-5}	7.40×10^{-5}	8.90×10^{-5}	2.37×10^{-4}

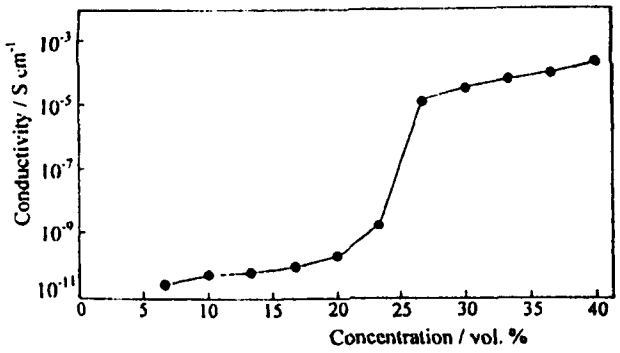

Fig. 5. Variation of conductivity for the polypyrrole/polyantimonic acid composites (HCl treated) with concentration of pyrrole.

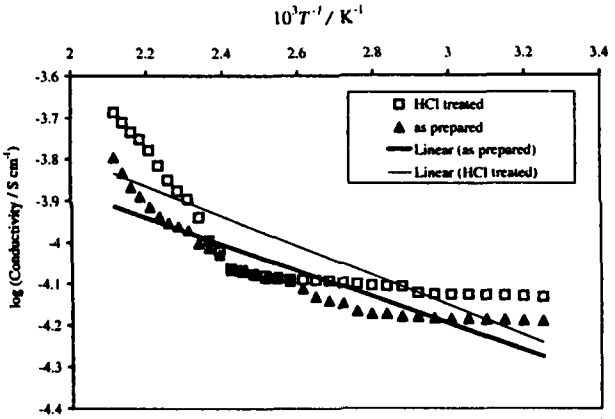

Fig. 6. Arrhenius plots for polypyrrole/polyantimonic acid composite material.

tivity is quite stable at 50, 70, 90 and 110 °C, which supports the fact that the dc electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150 °C, which may be attributed to the loss of dopant and the chemical reaction of dopant with the material.

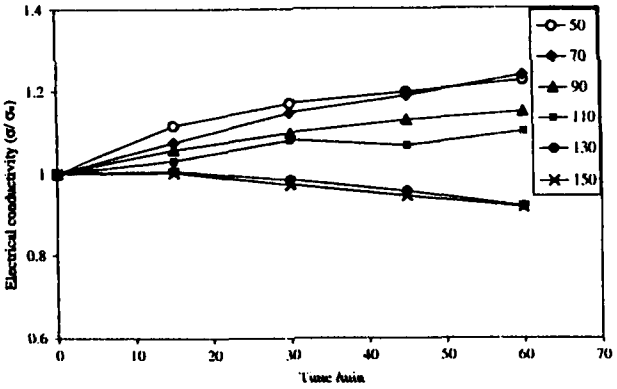

Fig. 7. Isothermal stability of polypyrrole/polyantimonic acid composite (HCl treated) in terms of retention of dc electrical conductivity with respect to time at 50, 70, 90, 110, 130 and 150 °C.

The stability of the material (HCl treated) in terms of electrical conductivity retention was also monitored for five cycles by repeated linear four-probe dc electrical conductivity measurements for increasing temperatures at 1 h intervals, and the dc conductivity for each heating cycle was plotted as $\log\sigma$ versus $1000/T$ (T in K) as shown in Fig. 8. It was observed that the temperature dependence of each plot followed the Arrhenius equation. There were only minor differences in the electrical conductivities even after repeating the experiment five times, which showed the good stability of the material during the heating-cooling cycles under severe oxidizing conditions up to 200 °C. The material was also observed to be a stable material, i.e., the room temperature conductivity is negligibly affected by short-term exposure to laboratory air as is evident from Fig. 9.

Table 2
Electrical conductivity of different forms of polypyrrole/polyantimonic acid composite at room temperature (prepared with 33.33% pyrrole monomer)

Sample number	Polypyrrole/polyantimonic acid composites	10^3 Conductivity (S cm^{-1})
1	As prepared	6.43
2	HCl treated	7.33
3	NaCl treated	6.95
4	KCl treated	6.70
5	LiCl treated	7.19
6	$CaCl_2$ treated	53.1

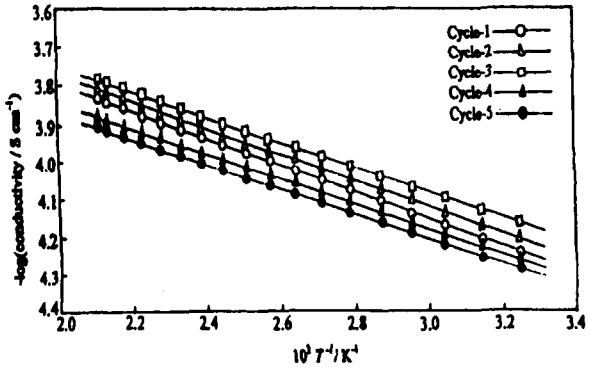

Fig. 8. Arrhenius plot of retention of dc electrical conductivity for polypyrrole/polyantimonic acid (HCl treated) during heating-cooling cycles up to 200 °C.

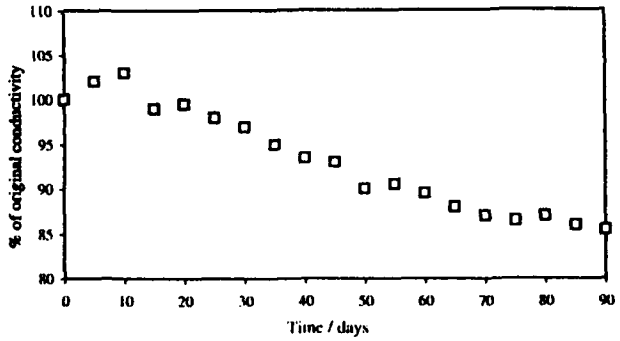

Fig. 9. Conductivity versus time of exposure to laboratory air for polypyrrole/polyantimonic acid composite material (HCl treated).

3.3. Ion-exchange kinetics of polypyrrole/polyantimonic acid composite

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Mg(II) H(I), Ca(II) H(I), Sr(II)–H(I), Ba(II)–H(I), Ni(II)–H(I), Cu(II)–H(I), Mn(II)–H(I) and Zn(II)–H(I). The particle diffusion-controlled phenomenon is favored by a high metal ion concentration, a relatively large particle size of the exchanger and vigorous shaking of the exchanging mixture.

The infinite time of exchange is the time necessary to obtain equilibrium in an ion exchange process. The ion-exchange rate becomes independent of time after this interval. Fig. 10 shows that 25 min were required for the establishment of equilibrium at 33 °C for Mg^{2+}–H^+ exchange. Similar behavior was observed for Ca^{2+}–H^+, Sr^{2+}–H^+, Ba^{2+}–H^+, Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+ exchanges. Therefore, 25 min was assumed to be the infinite time of exchange for the system. A study of the concentration effect on the rate of exchange at 33 °C showed that the initial rate of exchange was proportional to the metal ion concentration at

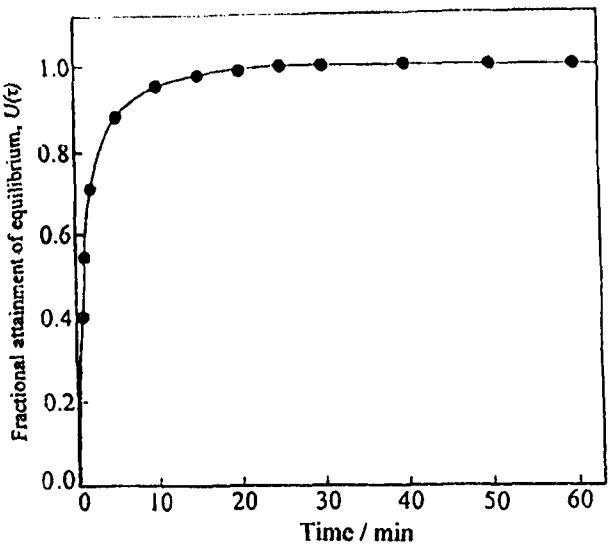

Fig. 10. A plot of $U(\tau)$ versus t (time) for M(II)–H(I) exchanges at 33 °C on a polypyrrole/polyantimonic acid composite cation-exchanger for the determination of infinite time.

and above 0.02 M (Fig. 11). Below the concentration of 0.02 M, film diffusion control was more prominent.

The results are expressed in terms of the fractional attainment of equilibrium, $U(\tau)$ with time according to the equation

$$U(\tau) = \frac{\text{the amount of exchange at time } 't'}{\text{the amount of exchange at infinite time}} \quad (4)$$

Plots of $U(\tau)$ versus time (t) (t in min), for all metal ions (Fig. 12) indicated that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with an increase in temperature and the uptake decreased with time. Each value of $U(\tau)$ will have a corresponding va-

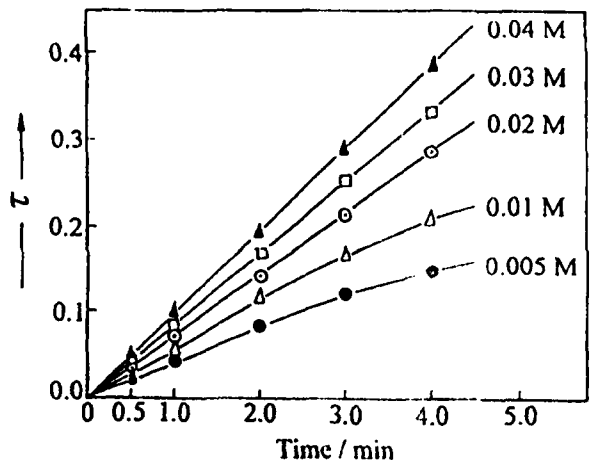

Fig. 11. A plot of τ versus t (time) for M(II)–H(I) exchanges using different metal solution concentrations at 33 °C on a polypyrrole/polyantimonic acid composite cation-exchanger.

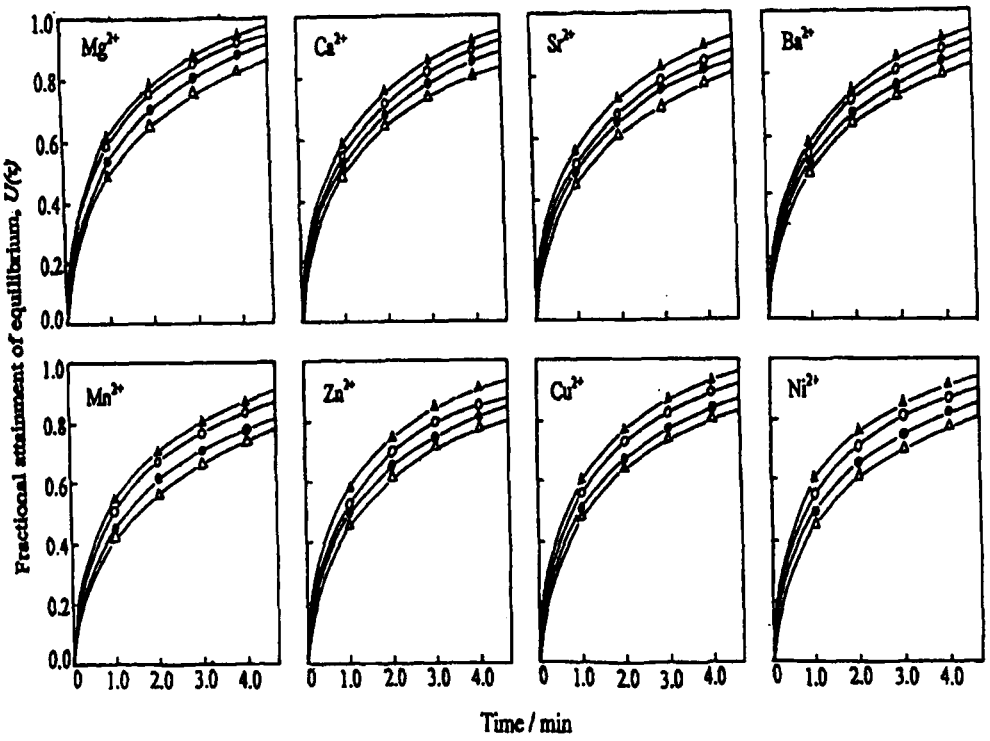

Fig. 12. Plots of $U(\tau)$ versus t (time) for different M(II)–H(I) exchanges at different temperatures on a polypyrrole/polyantimonic acid composite cation-exchanger: (Δ) 25 °C; (●) 33 °C; (O) 50 °C; (▲) 65 °C.

lue of τ, a dimensionless time parameter. On the basis of the Nernst–Planck equation, the numerical results can be expressed by explicit approximation [60–62]

$$U(\tau) = \{1 - \exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2}, \quad (5)$$

where τ is the half time of exchange $= \bar{D}_{H^+}t/r_0^2$, α is the mobility ratio $= \bar{D}_{H^+}/\bar{D}_{M^{2+}}$, r_0 is the particle radius, $\bar{D}_{H^+}$ and $\bar{D}_{M^{2+}}$ are the inter diffusion coefficients of counter ions H^+ and M^{2+}, respectively, in the exchanger phase. The three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ depend upon the mobility ratio (α) and the charge ratio $(Z_{H^+}/Z_{M^{2+}})$ of the exchanging ions. Thus they have different expressions as given below. When the exchanger is taken in the H^+-form and the exchanging ion is M^{2+}, for $1 \leqslant \alpha \leqslant 20$, as in the present case, the three functions have the values:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36\alpha^{0.668}},$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0\alpha^{0.4635}},$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09\alpha^{1.140}}.$$

The value of τ is obtained on solving Eq. (5) using a computer. The plots of τ versus time (t) at the four temperatures, as shown in Fig. 13, are straight lines passing through the origin, confirming the particle dif-

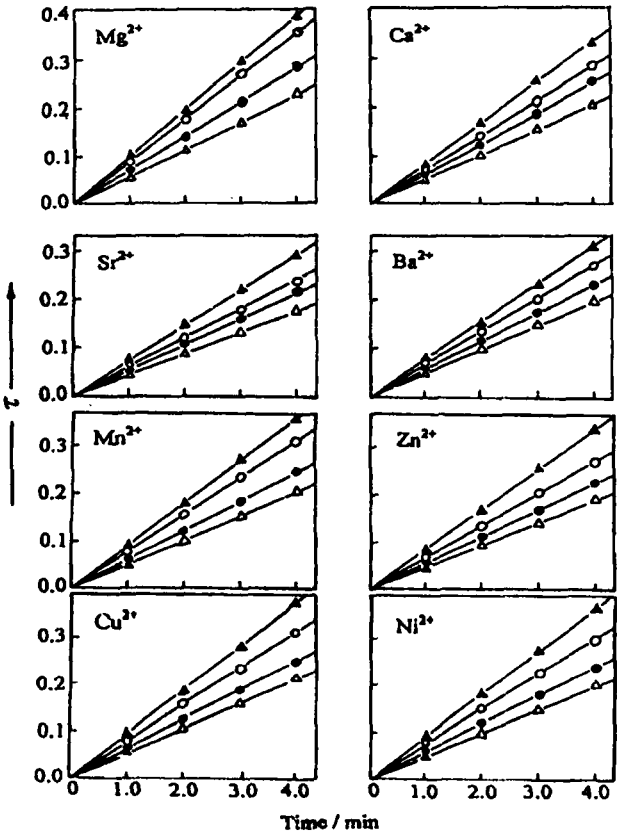

Fig. 13. Plots of τ versus t (time) for different M(II)–H(I) exchanges at different temperatures on a polypyrrole/polyantimonic acid composite cation-exchanger: (Δ) 25 °C; (●) 33 °C; (O) 50 °C; (▲) 65 °C.

Table 3
Slopes of various τ versus time (t) plots on polypyrrole/polyantimonic acid at different temperatures

Migrating ions	10^4 S (s^{-1})			
	25 °C	33 °C	50 °C	65 °C
Mg(II)	9.53	11.88	14.93	16.37
Ca(II)	8.59	10.25	11.72	13.88
Sr(II)	7.38	8.98	9.77	12.23
Ba(II)	8.20	9.65	11.18	12.89
Cu(II)	8.78	10.25	12.89	15.41
Ni(II)	8.15	9.94	12.36	15.10
Zn(II)	7.85	9.33	11.27	13.92
Mn(II)	8.44	10.13	12.91	14.87

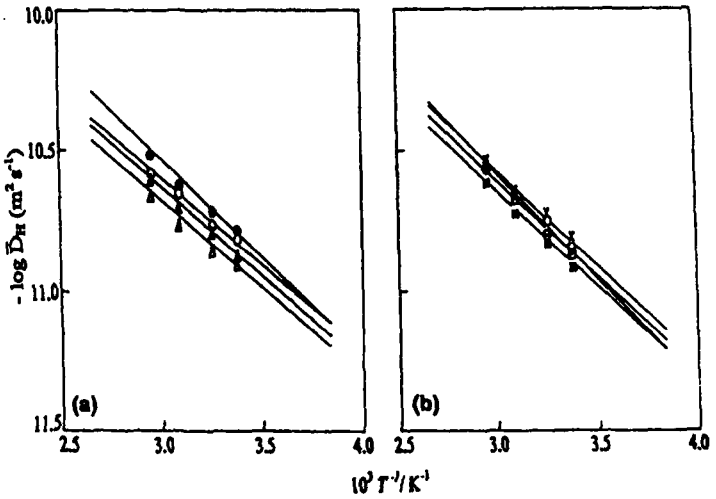

Fig. 14. Plots of $-\log \bar{D}_{H}$ versus 1000/T (T in K) for (a) Mg (II): ●, Ca(II): ○, Ba(II): ▲, Sr(II): △, and (b) Mn(II): □, Ni(II): ⊙, Cu(II): ×, Zn(II): ■, on a polypyrrole/polyantimonic acid composite cation-exchanger.

fusion control phenomenon for M(II)–H(I) exchanges at a metal ion concentration of 0.02 M.

The slopes (S values) of various τ versus time (t) plots are given in Table 3. The S values are related to $\bar{D}_{H^+}$ as follows:

$$S = \bar{D}_{H^+}/r_0^2. \quad (6)$$

The values of $-\log \bar{D}_{H^+}$ obtained by using Eq. (6) plotted against $1/T$ are straight lines as shown in Fig. 14, thus verifying the validity of the Arrhenius relation

$$\bar{D}_{H^+} = D_0 \exp(-E_a/RT). \quad (7)$$

D_0 is obtained by extrapolating these lines and using the intercepts at the origin. The activation energy (E_a) is then calculated with the help of the Eq. (7), putting the value of $\bar{D}_{H^+}$ at 273 K. The entropy of activation (ΔS^*) was then calculated by substituting D_0 in Eq. (8)

Table 4
Values of D_0, E_a and ΔS^* for the exchange of H(I) with some metal ions on polypyrrole/polyantimonic acid composite cation-exchange material

Metal ion exchange with H(I)	10^9 Ionic mobility ($m^2 V^{-1} s^{-1}$)	10^2 Ionic radii (nm)	10^{10} D_0 ($m^2 s^{-1}$)	E_a (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
Mg(II)	55	7.8	17.0	4.11	−113.33
Ca(II)	62	10.6	9.77	5.14	−71.00
Sr(II)	62	12.7	9.71	5.16	−70.47
Ba(II)	66	14.3	9.33	5.12	−67.47
Cu(II)	57	7.0	12.6	9.23	−90.40
Ni(II)	52	7.8	13.8	8.47	−97.46
Zn(II)	56	8.3	12.1	8.72	−87.41
Mn(II)	55	9.1	20.8	6.44	−128.68

$$D_0 = 2.72d^2(kT/h)\exp(\Delta S^*/R), \quad (8)$$

where d is the ionic jump distance taken as 5 Å [63], k is the Boltzmann constant, R is the gas constant, h is Plank's constant and T is taken as 273 K. The values of the diffusion coefficient (D_0), energy of activation (E_a) and entropy of activation (ΔS^*) thus obtained are summarized in Table 4.

The kinetic study reveals that equilibrium is attained faster at a higher temperature (Fig. 12), probably because of a higher diffusion rate of ions through the thermally enlarged interstitial positions of the ion-exchange matrix. The particle diffusion phenomenon is evident from the straight lines passing through the origin for the τ versus time (t) plots, as shown in Fig. 13. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange [M(II)–H(I)] process.

4. Conclusion

Inorganic precipitate polyantimonic acid modified by incorporation of polypyrrole behaves as an electrically conducting composite cation-exchanger. The electrical semiconducting behavior of this polymeric-inorganic hybrid material can be employed as a semiconductor in electrical and electronic devices. The feasibility of ion-exchange behavior has also been justified by determining various physical parameters in kinetic studies. The chemical, thermal and mechanical strength of this electroactive material can be utilized to make its ion-selective membrane electrode for the selective determination and separation of heavy metal ions in the solutions. It is highly selective for Mercury (a major hazardous toxic element in the environment), as shown from the selectivity studies [3] performed in our laboratory, which makes it important for the environmentalists. Compared to other ion-exchange materials of this class, it offers good environmental and economical advantages.

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Synthesis, characterization and ion-exchange properties of a new and novel 'organic–inorganic' hybrid cation-exchanger: Nylon-6,6, Zr(IV) phosphate

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Abstract

Organic–inorganic hybrid materials enable the integration of useful organic and inorganic characteristics within a single molecular-scale composite. Unique ion-exchange properties of these types of materials have been observed, and many others can be envisioned for this promising class of materials. In this paper, we describe the ion-exchange and physico-chemical properties of one family of self-assembling organic–inorganic hybrid based on nylon-6,6, framework with Zr(IV) phosphate an inorganic ion-exchanger. The physico-chemical properties of this hybrid material were determined using atomic absorption spectrophotometry (AAS), CHN elemental analysis, ICP–MS, UV–vis spectrophotometry, FTIR, TGA–DTA and scanning electron microscope (SEM) studies. Ion-exchange capacity (IEC), thermal stability and distribution behavior, *etc.* were also carried out to understand the cation-exchange behavior of the material. On the basis of distribution studies, the material was found to be highly selective for Hg(II), a highly toxic environmental pollutant. Its selectivity was examined by achieving some important binary separations like Hg(II)–Mg(II), Hg(II)–Zn(II), Hg(II)–Fe(III), Hg(II)–Bi(III), *etc.* Thus, the relatively new field of "organic–inorganic" hybrids offers a variety of exciting technological opportunities to decrease the environmental pollution.

Keywords: Organic–inorganic hybrid; Cation-exchanger; Nylon-6,6; Zr(IV) phosphate

1. Introduction

Wastewater containing heavy metals is generated, as untreated or partially treated by-product of various industries enter into public sewers, rivers, sea and on land. Heavy metals when present in water in concentrations exceeding the permitted limits are injurious to the health. Hence, it is very important to treat such waters to remove the metal ions present before it is supplied for any useful purpose. Therefore, many investigations have studied to develop more effective process to treat such waste stream. Ion-exchange has been widely adopted in heavy metal containing wastewater and most of the ion-exchangers (*i.e.* ion-exchange media) currently being used are commercially mass-produced organic resins [1].

Although the organic ion-exchangers have a wide applicability, a few limitations of the organic resins have been reported. One of the severest limitations of the organic resin is its poor thermal stability; for instance, the mechanical strength and removal capacity of ordinary organic ion-exchange resins tend to decrease under high temperature conditions which are frequently encountered in processing liquid radioactive waste stream [1,2]. Since organic ion-exchangers were found to be unstable at high temperature and under strong radiation, inorganic ion-exchanger were taken as alternatives for such cases. However, the inorganic adsorbents have their own limitations. For instance, these materials, in general are reported to be not very much reproducible in behavior and fabrication of the inorganic adsorbents into rigid beads type media suitable for column operation is quite difficult. Further, they have generally worse mechanical and chemical strength than the organic counterpart because of their inorganic nature [3].

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In order to overcome the above limitations of organic resins and inorganic adsorbents, many investigators have introduced organic–inorganic hybrid ion-exchangers consisting of inorganic ion-exchangers and organic binding matrices [4–14]. These materials have conjugate the mechanical properties of the organic polymers with the intrinsic properties of the inorganic compound creating a new class of hybrid organic–inorganic materials with improvement in mechanical properties, chemical inertness, high temperature and radiation stability, reproducibility and high selectivity for heavy metal ions.

'Organic–inorganic' hybrid materials prepared by sol–gel approach have attracted a great deal of attentions in material science. The synthesis of hybrid ion-exchangers with controlled functionality and hydrophobicity could open new avenues for organometallic chemistry, catalysis, organic host guest chemistry [15–17], analytical chemistry, hydrometallurgy, antibiotic purification and separation of radioactive isotopes, and find large scale application in water treatment and pollution control [18,19]. Thus, organic–inorganic hybrid materials are expected to provide many possibilities as new composite materials. The hybrid materials usually show properties intermediate between those of plastics and glasses (ceramics). Accordingly, hybrid can be used to modify organic polymer materials or to modify inorganic glassy materials. In addition of these characteristics, the hybrid materials can be considered as a new composite materials that exhibit very different properties from their original components (organic polymer and inorganic materials), especially in the case of molecular level hybrids. Thus, the synthesis of polymeric/inorganic composites has received a great deal of attention because it provided new materials with special mechanical, chemical, electrochemical and optical as well as magnetic properties [20–25].

In the present study, we have chosen the synthesis, characterization, ion-exchange studies and analytical application of organic–inorganic hybrid cation-exchanger by the incorporation of organic polymer, *i.e.* nylon-6,6, and inorganic ion-exchanger, 'Zr(IV) phosphate' by simultaneous gelation of inorganic acid salt as well as by dissolving nylon-6,6, in acidic media using formic acid.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, GSC, E-merck, Qualigens (India). All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India), a FTIR spectrophotometer (Perkin-Elmer Spectrum-BX, U.S.A.), an automatic thermal analyzer (V2.2A Du Pont 9900), an elemental analyzer (Carlo-Erba 1180), a double beam atomic absorption spectrophotometer (GBC 902, Australia), an inductively coupled plasma mass spectrophotometer, an electron microscope (LEO 435 VP, Australia) with attached imaging device, a UV–vis spectrophotometer (Elico EI 301E, India) and a water bath incubator shaker were used.

2.2. Preparation of reagents

Solution of (0.10 mol dm^{-3}) zirconyl oxychloride, $ZrOCl_2 \cdot 8H_2O$ was prepared in 1.0 mol dm^{-3} HCl, while orthophoric acid, H_3PO_4 solutions of different molarities were prepared in demineralized water (DMW). Different weight of nylon-6,6, were dissolved in different volume of concentrated formic acid.

2.3. Preparation of nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger

Inorganic precipitates of zirconiun(IV) phosphate were prepared by adding 0.10 mol dm^{-3} zirconyl oxychloride ($ZrOCl_2 \cdot 8H_2O$) solution prepared in 1.0 mol dm^{-3} HCl at the flow rate of 0.50 cm^3 min^{-1} to solutions of H_3PO_4 of different molarities, *viz.* 0.50, 1.0, 1.50, 2.0 mol dm^{-3}. The white precipitates were obtained, when the pH of the mixtures was adjusted 1.0 by adding aqueous ammonia with constant stirring. The gels of nylon-6,6, prepared in concentrated formic acid were added into the white inorganic precipitate of Zr(IV) phosphate and mixed thoroughly with constant stirring. These slurries were refluxed for 2 h at a temperature of 60 ± 5 °C and were kept for 24 h at room temperature (25 ± 2 °C) for digestion. The supernatant liquid was decanted and gels were filtered by suction and the excess acid was removed by several washings with DMW and the materials were dried in an air oven over P_4O_{10} at 40 °C. The dried products were immersed in DMW to obtain small granules. They were converted to H^+-form by treating with 1.0 mol dm^{-3} HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid. The excess acid was removed after several washings with DMW, dried at 50 °C and sieved to obtain particles of particular size range (~125 μm) and kept in desiccators.

Hence, a number of samples of 'nylon-6,6, Zr(IV) phosphate' hybrid cation-exchanger were prepared (Table 1) and on the basis of Na^+ ion-exchange capacity (IEC), percentage of yield and physical appearance of beads, sample S-7 was selected for detailed studies.

2.4. Ion-exchange capacity

One gram (1.0 g) of the dry cation-exchanger, sample S-7 in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~1.0×10^{10} pm and fitted with glass wool support at the bottom. The bed length was approximately 1.50×10^{10} pm long. 1.0 mol dm^{-3} alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the nylon-6,6, Zr(IV) phosphate cation-exchange column, maintaining a very slow flow rate (~0.50 cm^3 min^{-1}). The effluent was titrated against a standard 0.10 mol dm^{-3} NaOH solution using phenolphthalein indicator.

2.5. Thermal effect on ion-exchange capacity

To study the effect of drying temperature on the IEC, 1.0 g samples of the organic–inorganic hybrid cation-exchange mate-

Table 1
Conditions of preparation of various samples of nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger

Sample no.	Mixing volume ratio (v/v) $ZrOCl_2 \cdot 8H_2O$ in 1 mol dm^{-3} HCl	H_3PO_4 in DMW (mol dm^{-3})	pH of the inorganic precipitate	w/v ratio		Appearance of beads after drying	Na^+ ion-exchange capacity (m mol g^{-1})
				Nylon-6,6	Formic acid		
S-1	4.0	1.0 (1.0)	1.0	1.00	1.0	White granular	1.40
S-2	4.0	2.0 (1.0)	1.0	1.00	1.0	"	1.70
S-3	4.0	3.0 (1.0)	1.0	1.00	1.0	"	1.44
S-4	4.0	1.0 (2.0)	1.0	0.50	1.0	"	1.48
S-5	4.0	2.0 (2.0)	–	0.50	1.0	"	1.50
S-6	4.0	3.0 (2.0)	1.0	0.75	–	"	1.60
S-7	4.0	4.0 (2.0)	1.0	1.00	1.0	"	1.80
S-8	4.0	4.0 (2.0)	1.0	–	–	"	1.22
S-9	4.0	5.0 (2.0)	1.0	1.25	1.0	"	1.65
S-10	4.0	3.0 (1.50)	1.0	1.00	1.0	"	1.50
S-11	4.0	4.0 (1.50)	1.0	1.00	1.0	"	1.70
S-12	4.0	1.0 (0.50)	1.0	1.00	1.0	"	1.48
S-13	4.0	1.5 (0.50)	1.0	1.00	2.0	"	1.15
S-14	4.0	2.0 (0.50)	1.0	1.00	2.0	"	1.20

rial (S-7) in the H^+-form were heated at various temperatures in a muffle furnace for 1 h and the Na^+ ion-exchange capacity was determined by column process after cooling them at room temperature.

2.6. *Effect of eluant concentration*

To find out the optimum concentration of the eluant for complete elution of H^+ ions, a fixed volume (250 cm^3) of $NaNO_3$ solution of varying concentrations ranging from 0.20 to 1.40 mol dm^{-3} with a unit difference of 0.20 mol dm^{-3} were passed through a column containing 1.0 g of the cation-exchange material (S-7) in the H^+-form with a flow rate of ~0.50 cm^3 min^{-1}. The effluent was titrated against a standard alkali solution of 0.10 mol dm^{-3} NaOH for the H^+ ions eluted out.

2.7. *Elution behavior*

To find out the efficiency of column containing 1.0 g of the cation-exchanger (S-7) in H^+-form was eluted with 1.0 mol dm^{-3} $NaNO_3$ solution of this concentration in different 10.0 cm^3 fractions with minimum flow rate as described above. Each fractions of 10.0 cm^3 effluent was titrated against a standard alkali solution for the H^+ ions eluted out.

2.8. *pH-titration*

pH-titration studies of nylon-6,6, Zr(IV) phosphates (S-7) were performed by the method of Topp and Pepper [26]. A total of 1.0 g portions of the cation-exchanger in the H^+-form were placed in each of the several 250 cm^3 conical flasks, followed by the addition of equimolar solutions of alkali metal chlorides and their hydroxides in different volume ratio, the final volume being 50 cm^3 to maintain the ionic strength constant. The pH of the solution was recorded after every 24 h until equilibrium was attained, which needed ~5 days and pH at equilibrium was plotted against the m moles of OH^- ions added.

2.9. *Chemical composition*

To determine the chemical composition of 'nylon-6,6, Zr(IV) phosphate' (sample S-7), 0.20 g of the sample was dissolved in 20 cm^3 of concentrated H_2SO_4. The material was analyzed for 'Zr(IV)' by ICP–MS and phosphate by the phosphovanado molybdate method [27]. Carbon, hydrogen and nitrogen contents of the cation-exchanger were determined by elemental analysis. The weight percent composition of the material was: Zr, 20.09; P, 13.70; C, 31.75; H, 6.80; N, 6.20; O, 21.46.

2.10. *Thermogravimetric analysis (TGA) study*

Thermogravimetric study was also carried out on heating the sample material S-7 (as-prepared) up to 900 °C at a constant rate (~10 °C min^{-1}) in the air atmosphere.

2.11. *FTIR studies*

The FTIR spectrum of Zr(IV) phosphate (S-6) and nylon-6,6, Zr(IV) phosphate (S-7) (as-prepared) dried at 50 °C was taken by KBr disc method.

2.12. *Scanning electron microscopy (SEM) studies*

SEM was performed on ground materials (as-prepared) by an electron microscope at various magnifications.

2.13. *Distribution (sorption) studies*

The distribution coefficient (K_d values) of various metal ions on nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger was determined by batch method in various solvent systems. Vari-

ous 0.20 g of the composite cation-exchanger beads (S-7) in the H^+ ion form were taken in 20.0 cm^3 of different metal nitrate solutions in the required medium and kept for 24 h with continuous shaking for 6 h in a temperature controlled incubator shaker at 25 ± 2 °C to attain equilibrium. The initial metal ion concentration was to adjust that it did not exceed 3.0% of its total ion-exchange capacity. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.0050 mol dm^{-3} solution of EDTA [28] and some heavy metal ions such as [Pb^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}] were determined by atomic absorption spectrophotometry (AAS). The distribution coefficient (K_d) values were calculated using the formula given below:

$$K_d = \frac{I - F}{F} \times \frac{V}{M} (\text{ml g}^{-1}) \quad (1)$$

where I is the initial amount of the metal ion in the solution phase, F final amount of metal ion in the solution phase, V the volume of the solution (cm^3) and M the amount of exchanger (g).

2.14. Quantitative separation of metal ions

Quantitative binary separations of some important metal ions were achieved on the proposed hybrid cation-exchanger column. 1.0 g of the cation-exchanger, S-7 (~125 μm) in H^+-form were used for column separations in a glass tube having an internal diameter of $\sim 0.60 \times 10^{10}$ pm and a height of 35.0×10^{10} pm. The column was washed thoroughly with DMW and the mixture of two metal ions having initial concentrations of 0.010 mol dm^{-3} each, to be separated was loaded on it and allowed for 1 h to absorb the metal ions on the exchanger and pass on to the column gently (maintaining a flow rate of 2–3 drops min^{-1}) till the level was above the surface of the material. After recycling two or three times to ensure complete absorption of the mixture on column beads, the separation was achieved by passing a suitable solvent at a flow rate of 1.0 cm^3 min^{-1} through the column as eluent. The metal ions in the effluent were determined quantitatively by AAS and EDTA titration [28].

3. Results and discussions

In this study, various samples of new and novel hybrid cation-exchanger nylon-6,6, Zr(IV) phosphate were prepared by sol–gel mixing of inorganic precipitate of zirconium(IV) phosphate and nylon-6,6, dissolved in formic acid in different mixing (w/v) ratio's as given in Table 1. This cation-exchanger appears to be a promising hybrid material with good ion-exchange capacity, thermal, mechanical, and chemical stability. The improvement in these characteristics of organic–inorganic hybrid cation-exchanger may be due to the binding of organic polymeric material with inorganic moiety. The most interesting characteristics of this hybrid material is its granulometric property, showing a good reproducible behavior as is evident from the fact that these materials obtained from various batches did not show any appreciable deviation in their percentage of yield and ion-exchange capacities. The effect of the size and charge of the exchanging ion on the ion-exchange capacity was also observed for this hybrid material. The ion-exchange capacity of the hybrid cation-exchanger for alkali ions and alkaline earth metal ions increases according to the decrease in the hydrated ionic radii [29–32] as evident from Table 2. These results were also similar as reported by Nachod and Wood [33] for the exchange of alkali and alkaline earth metal ions on carbonaceous zeolites.

Table 2
Ion-exchange capacity of various exchanging ions on a hybrid cation-exchanger nylon-6,6, Zr(IV) phosphate

Exchanging ions	pH of the metal solutions	Ionic radii (Å)	Hydrated ionic radii (Å)	IEC (m mol g^{-1})
Li^+	6.70	0.68	3.40	1.63
Na^+	6.70	0.97	2.76	1.80
K^+	6.80	1.33	2.32	1.90
Mg^{2+}	6.50	0.78	7.00	1.35
Ca^{2+}	6.50	1.06	6.30	1.55
Sr^{2+}	6.30	1.27	–	1.64
Ba^{2+}	6.30	1.43	5.90	1.73

Effect of heating at different temperature for 1 h, indicated that on heating at elevated temperature the mass, physical appearance and ion-exchange capacity of the dried hybrid cation-exchanger (S-7) was changed as the temperature increased as shown in Table 3. It was also observed that the hybrid cation-exchanger possessed higher thermal stability as the sample maintained about 80.0% of the initial mass by heating up to 400 °C. However, in terms of ion-exchange capacity, this hybrid material was found stable up to 150 °C and it retained about 72.22% of the initial ion-exchange capacity by heating up to 350 °C (Table 3).

The rate of elution is governed by the concentration of the eluent, which was found as an usual behavior for these types of ion-exchange materials. The minimum molar concentration of $NaNO_3$ as eluent for nylon 6,6, Zr(IV) phosphate (S-7) was found 1.0 m dm^{-3}, for maximum release of H^+ ions from 1.0 g of the cation-exchanger as evident from Fig. 1.

The efficiency of 1.0 g hybrid cation-exchanger column determined by the elution behavior indicate that the exchange is quite fast as at the beginning all the exchangeable H^+ ions are eluted out in the first 150 cm^3 of the effluent (Fig. 2) within 5 h.

Table 3
Effect of temperature on ion-exchange capacity of nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger on heating time for 1 h

Heating temperature (°C)	Appearance (color)	Weight loss (%)	Na^+ ion-exchange capacity (m mol g^{-1})	% Retention of IEC
50	White granular	–	1.80	100.00
100	"	5.45	1.80	100.00
150	Brown	10.35	1.80	100.00
200	"	14.11	1.50	83.33
300	"	17.30	1.43	79.44
350	Gray	17.45	1.32	72.22
400	Dark gray	20.00	0.95	52.77

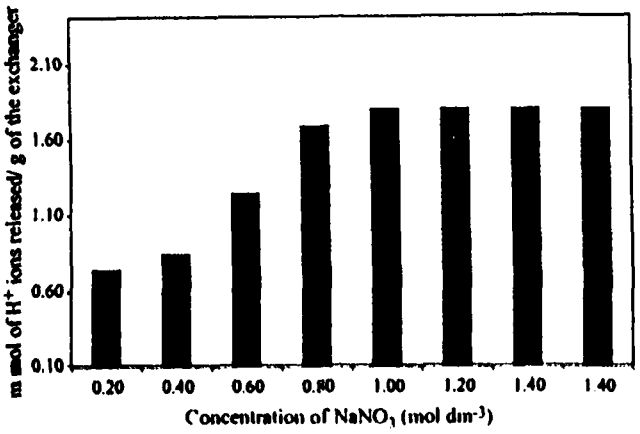

Fig. 1. Effect of eluent concentration on ion-exchange capacity of nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger.

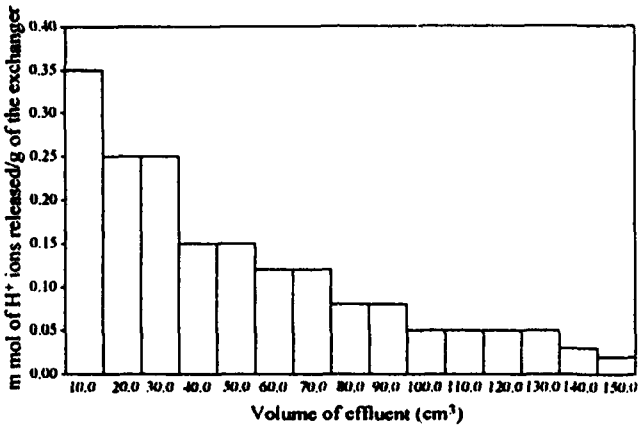

Fig. 2. Elution behavior of nylon-6,6, Zr(IV) phosphate hybrid cation-exchange material.

The pH-titration curve Fig. 3 showed slow increase when NaOH, KOH and LiOH were added 0.50–1.50 m mol g^{-1} of cation-exchanger, and relatively very slow steep increase when these hydroxides were added 1.50–2.0 m mol g^{-1} of cation-exchanger. This composite cation-exchanger may be a strong acid cation-exchanger because the pH-titration curve usually showed a step edge at 2.0 m mol g^{-1} of cation-exchanger that is, the –H functional groups on the hybrid cation-exchanger were depleted and replaced with Na^+, K^+ and Li^+ ions at that point and the number of –H sites were the same as the amount of NaOH, KOH and LiOH added. Thus, theoretical ion-exchange capacity of this hybrid cation-exchanger may be considered as 2.0 m mol g^{-1} of cation-exchanger. After that point, in the region when more NaOH, KOH and LiOH are added, the equilibrium pH further increases but more slowly. This slow increase of pH-titration curve after 2.0 m mol g^{-1} of cation-exchanger implies due to surface precipitation other than conventional ion-exchange or surface adsorption.

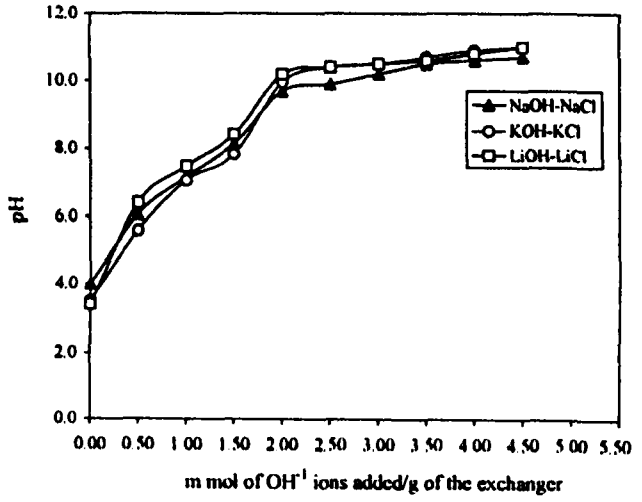

Fig. 3. pH-titration curves for nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger with various alkali metal hydroxides.

The molar ratio of Zr, P, C, H, N, and O in the material was estimated to be 1.0:2.02:12.01:30.66:2.01:6.09, which can suggest the following formula of the material:

$$[Zr(HPO_4)_2 \cdot (-CO-(CH_2)_4-CO-NH-(CH_2)_6-N-)] \cdot nH_2O$$

Assuming that only the external water molecules are lost at 160 °C, the ~11.50 wt.% loss of mass represented by TGA curve must be due to the loss of nH_2O. Thus, from the above structure the value of 'n' the external water molecules can be calculated using Alberti's equation [34]:

$$18n = X\left(\frac{M + 18n}{100}\right) \quad (2)$$

where X is the percent weight loss (~11.50%) of the exchanger by heating up to 160 °C and $(M + 18n)$ is the molecular weight of the material. The calculations give ~4.0 for the external water molecule (n) per molecule of the cation-exchanger (sample S-7).

As evident from the thermogravimetric analysis curve (Fig. 4) of nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger initial weight loss of mass ~11.50% up to 160 °C, may be due to the loss of external water molecule present [35]. Slow weight loss observed between 160 °C and 320 °C may be due to the condensation of phosphate group to pyrophosphate groups. Further weight loss between 320 °C and 700 °C may be due to complete decomposition of the organic part of the material. At 700 °C onwards, a smooth horizontal section which represents the complete formation of the oxide form of the material.

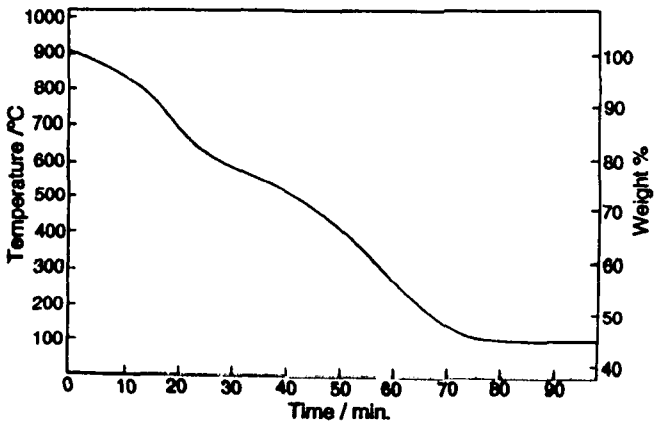

Fig. 4. Thermogravimetric (TGA) curve of nylon-6,6, Zr(IV) phosphate (as-prepared).

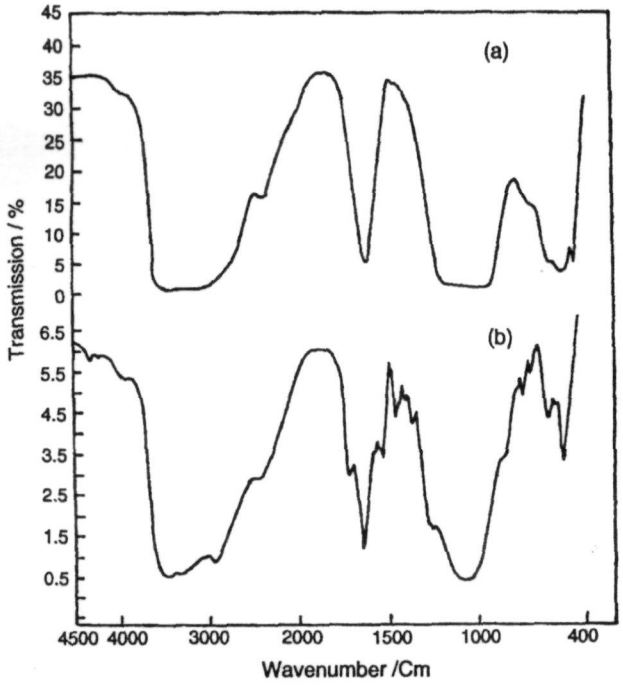

Fig. 5. FTIR spectra of as-prepared Zr(IV) phosphate (a) and nylon-6,6, Zr(IV) phosphate hybrid cation-exchange material (b).

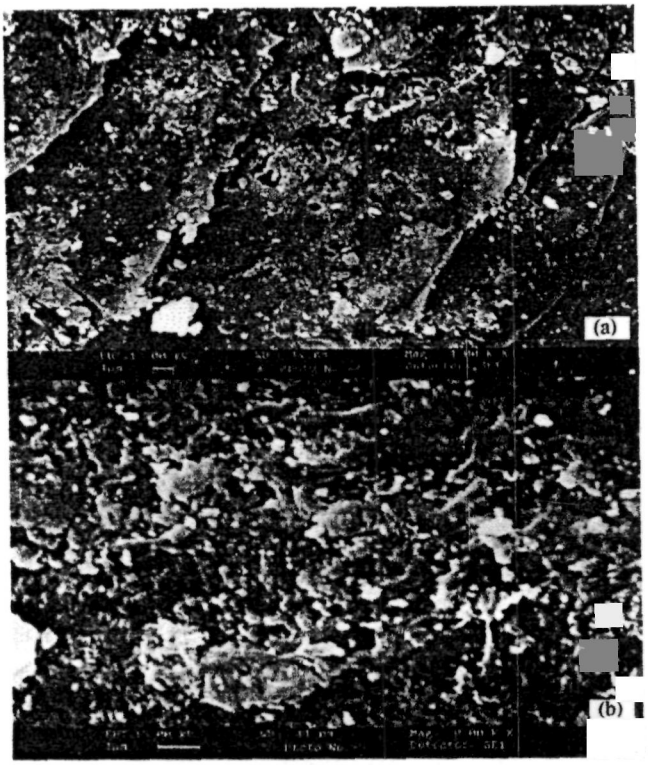

Fig. 6. Scanning electron microphotographs (SEM) of chemically prepared Zr(IV) phosphate at the magnification of 4.00 k× (a) and nylon-6,6, Zr(IV) phosphate hybrid system at the magnification of 8.00 k× (b).

The FTIR spectrum of hybrid cation-exchange material nylon-6,6, Zr(IV) phosphate (Fig. 5b) revealed the presence of the external water molecules in addition to the metal-oxygen and metal –OH stretching band. In the spectrum a broad band in the region at 3482 cm^{-1} may be due to the presence of external water molecules. While a sharp peak in region 1640 cm^{-1} is the indication of the presence of water of crystallization. A less broad peak around in the region 1076 cm^{-1} may be due to the presence of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{2-}$ [36]. This hybrid cation-exchanger also showed a strong band at 1641 cm^{-1} corresponding to the carbonyl group of nylon-6,6 and a small peak in the region 1460 cm^{-1} as a band of medium intensity mainly due to the C–H bending of methylene groups of nylon-6,6, moiety [37]. The absorption band in the region 1515 cm^{-1} may be due to the –NH stretching frequency of amide group of nylon-6,6 [38]. An assembly of two sharp peaks in the region 500–750 cm^{-1} is due to the superposition of metal-oxygen stretching vibrations. These characteristic stretching frequencies are also in close resemblance with the inorganic precipitate, *i.e.* Zr(IV) phosphate (Fig. 5a) and nylon-6,6, Zr(IV) phosphate (Fig. 5b), indicating the binding of inorganic precipitate with organic polymer and formation of 'organic–inorganic' hybrid nylon-6,6, Zr(IV) phosphate.

Scanning electron microscope pictures (Fig. 6) showed the difference in surface morphology of inorganic ion-exchanger Zr(IV) phosphate (Fig. 6a) and organic–inorganic hybrid material nylon-6,6, Zr(IV) phosphate(IV) phosphate (Fig. 6b). It has been revealed that after binding of inorganic precipitate of Zr(IV) phosphate, with organic polymer morphology has been changed.

In order to explore the potentiality of this hybrid cation-exchange material in the separation of metal ions, distribution studies for 12 metal ions were performed in seven solvent systems (Table 4). The distribution studies showed that the material was found to be the highly selective for Hg(II), which is a major polluting metal in the environment. The separation capacity of the material has been demonstrated by achieving some important binary separations such as Hg(II)–Mg(II), Hg(II)–Zn(II), Hg(II)–Fe(III), Hg(II)–Bi(III), *etc.* Table 5 summarizing the salient features of these separations. The separations are quite sharp and recovery is quantitative and reproducible. It was also

Table 4
K_d values of some metal ions on nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger column in different solvent systems

Metal ions	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10
Mg^{2+}	900	757	612	290	1135	975	625	1025	1112	396
Mn^{2+}	1100	1335	1249	812	935	655	420	735	620	316
Zn^{2+}	812	666	200	252	715	515	200	805	500	136
Pb^{2+}	1335	1152	1098	926	1400	1420	1309	1310	675	1105
Hg^{2+}	1500	928	928	466	1500	1500	1607	1600	1600	1000
Ni^{2+}	1166	840	695	190	928	323	189	750	500	189
Cu^{2+}	1300	888	785	163	1300	1300	265	785	500	300
Cd^{2+}	750	750	333	426	750	333	420	750	333	150
Co^{2+}	1375	1100	286	333	1375	571	1000	612	335	143
Fe^{3+}	1200	350	153	236	333	333	225	1200	600	150
Al^{3+}	1409	1120	750	312	1450	1201	1355	625	500	250
Bi^{3+}	935	725	616	425	1100	937	720	1300	765	225

Abbreviation: S-1, DMW; S-2, 10^{-3} mol dm^{-3} HNO_3; S-3, 10^{-2} mol dm^{-3} HNO_3; S-4, 10^{-1} mol dm^{-3} HNO_3; S-5, 10^{-3} mol dm^{-3} HCl; S-6, 10^{-3} mol dm^{-3} HCl; S-7, 10^{-2} mol dm^{-3} HCl; S-8, 10^{-1} mol dm^{-3} HCl; S-7, 0.10 mol dm^{-3} CH_3COOH + 0.10 mol dm^{-3} CH_3COONa (2:1); S-8, 0.10 mol dm^{-3} HNO_3 + 0.10 mol dm^{-3} NH_4NO_3 (1:1).

Table 5
Some binary separation of metal ions achieved on nylon-6,6, Zr(IV) phosphate hybrid cation-exchanger column

Separation achieved	Amount loaded (μg)	Amount found (μg)	% Error	Eluent used (mol dm^{-3})	Volume of eluent (cm^3)
Mg(II)	729 15	729 15	0 00	0 10 HNO_3	60
Hg(II)	2005 90	2005 90	0.00	0 10 HNO_3 + 0 10 NH_4NO_3 (1 1)	50
Zn(II)	980 55	983 82	+0.33	0 10 HNO_3 + 0 10 NH_4NO_3 (1 1)	50
Hg(II)	2005 90	1995 87	0 50	0 01 HNO_3	50
Fe(III)	1396 16	1396 16	0.00	0 10 HCl	60
Hg(II)	3008 85	2998 82	−0.33	0 10 HNO_3	50
Bi(III)	2089 80	2121 15	+1 48	0 10 HNO_3 + 0 10 NH_4NO_3 (1 1)	50
Hg(II)	3510 33	3490 27	−0 57	0 10 HNO_3	50
Mg(II)	850 66	849 45	−0 14	0 10 HNO_3	60
Pb(II)	4144 00	4144 00	0 00	0 10 CH_3COOH + 0 10 CH_3COONa (2 1)	50
Zn(II)	1307 40	1310 67	+0 25	0 10 HNO_3 + 0 10 NH_4NO_3 (1 1)	60
Pb(II)	3108 00	3097 64	−0 33	0 10 CH_3COOH + 0 10 CH_3COONa (2 1)	50

observed from the distribution studies that this hybrid cation-exchanger is also highly selective for Pb(II). Some binary separations (Pb^{2+}–Mg^{2+}, Pb^{2+}–Zn^{2+}), involving Pb(II) was also carried out on the proposed hybrid cation-exchanger column.

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